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By William A. Noyes, Edward Hart, W. F. Hillebrand, J. H. Long, Wm. McMurtrie, Arthur A. Noyes, H. N. Stokes, H. P. Talbot, and H. W. Wiley,

Committee on Papers and Publications of the American Chemical Society.

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REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

Received November 14, 1904.

THE International Committee on Atomic Weights respectfully submits the following report, together with a table of atomic weights for use during 1905.

Most of the values recommended in our table are identical with those reported in former years, but a few changes seem to be needed. Other changes, which are suggested by recent investigations, are deferred until fuller information regarding their desirability shall have been received. During 1904 there has been great activity in the determination of atomic weights; and a summary of the more important researches may help to explain our reasons for changing or retaining hitherto accepted values. The researches to be considered are as follows:

Glucinum.—The atomic weight has been redetermined by Parsons.[1] Seven analyses of the acetylacetonate gave, in mean, Gl = 9.113. Nine analyses of the basic acetate gave exactly the same average. As the individual determinations range from 9.081 to 9.142, the figure 9.1 may evidently remain unchanged.

Indium.—The investigation by Thiel[2] shows that the atomic weight of indium is higher than had been supposed. Analyses of

[1] This Journal, **26**, 721.

[2] *Ztschr. anorg. Chem.*, **40**, 280.

the trichloride gave, in mean, In = 115.05. Analyses of the tribromide gave 114.81. With the oxide, unsatisfactory results were obtained. For present purposes the round number 115 may be adopted, although further investigation is promised by Thiel, and a research by Dennis and Geer is in progress.

Iodine.—In our former reports we have noted the uncertainty in the accepted atomic weight of iodine. Stas, by the synthesis of AgI, found I = 126.85. Scott, by the same general method, found I = 126.97, and Ladenburg, by measuring the ratio AgI:AgCl, obtained the value 126.96. Koethner and Aeuer,[1] from data given by several methods, including a repetition of Ladenburg's process, conclude that the atomic weight of iodine cannot be less than 126.963, but the full details of their investigation, at the date of writing this report, are unpublished. A more recent research by G. P. Baxter will soon appear,[2] in which the higher value for iodine is completely confirmed, both by Ladenburg's method and by that of Stas. Baxter's final value is I = 126.975, and there can now be no reasonable doubt that the Stas figure is too low. The number 126.97 is adopted in our table for O = 16, or 126.01 with hydrogen as unity.

Nitrogen.—The accepted value for the atomic weight of nitrogen, 14.04, is derived mainly from the work of Stas. Of late years, however, the study of gaseous densities has led several physicists, notably Rayleigh, Leduc, and Daniel Berthelot, to the belief that the true value is but little in excess of the round number 14. Guye[3] finds, from the density of nitrogen, the value 14.004. Still more recently, Guye and Bogdan,[4] by analysis of nitrous oxide, have found N = 14.007. Jaquerod and Bogdan[5] have also studied nitrous oxide volumetrically, and obtained the figure 14.019. In view of the discordance between the volumetric and the gravimetric data, it seems undesirable to make any change at present in the number assigned to nitrogen. Further investigation of this atomic weight is evidently needed.

Rubidium.—Atomic weight redetermined by Archibald[6] from

[1] *Ber. d. chem. Ges.*, **37**, 2536.

[2] Since writing the above, the paper referred to has been published in this Journal, **26**, 1577.

[3] *Compt. Rend.*, **138**, 1213.

[4] *Ibid.*, **138**, 1494.

[5] *Ibid.*, **139**, 49.

[6] *J. Chem. Soc.* (Lond.), **85**, 776.

analyses of the chloride and bromide. The final mean, derived from many concordant experiments, is Rb = 85.485. As some of the determinations are slightly higher than 85.5, that figure may be adopted as sufficiently accurate for all practical purposes.

Samarium.—Urbain and Lacombe,[1] by analyses of the octohydrated sulphate, find Sm = 150.34. A comparison of this figure with the older determinations justifies the use of 150.3 as the most probable value for this atomic weight. The same authors[2] have also determined the atomic weight of *europium*, and give the figure Eu = 151.79. It is desirable, however, to await more complete information about europium before recognizing it in the table.

Thorium.—Evidence as to the complex nature of ordinary "thorium" is steadily accumulating. According to Baskerville[3] it is a mixture of at least three elements, which he calls carolinium, thorium, and berzelium. Their approximate atomic weights are 256, 220, and 212.5, respectively, supposing them all to be tetrads. The value in our table is that of ordinary thorium, as it is found in mineral analyses, and no change can safely be made until our knowledge has become more definite.

Tungsten.—The figure commonly assigned to tungsten, W = 184, has been verified by Smith and Exner.[4] From 27 measurements of the ratio $WCl_5 : WO_3$, W = 184.04. From 23 syntheses of WO_3, W = 184.065. The individual determinations range from 183.94 to 184.14, which is a fair degree of concordance for so high an atomic weight.

Changes, then, are recommended in the cases of indium, iodine, rubidium and samarium. The column of atomic weights which referred to the hydrogen unit has also been carefully recalculated, and in it some small alterations appear. The latter modifications, however, are unimportant, except in so far as they help to bring the two tables into greater harmony.

During the year there has been a revival of the agitation over the question of standards, and the policy of this committee, or rather sub-committee of the larger international body, in publishing a double table, has encountered some criticism. That criticism is perfectly legitimate, and we are glad to say that it has been ex-

[1] *Compt. Rend.*, **138**, 1166.
[2] *Ibid.*, **138**, 627.
[3] This Journal, **26**, 922.
[4] *Proc. Am. Phil. Soc.*, **43**, 123; This Journal, **26**, 1082.

pressed courteously, and in a truly scientific spirit. Professors Sakurai and Ikeda[1] have published an open letter upon the subject,[2] and in response to a demand within the German Chemical Society, the committee representing that body issued a circular to the members of the larger International Committee, asking for an expression of opinion as to our procedure. We are not yet informed regarding the responses to that circular, and we therefore cannot base any action upon it. The Council of the American Chemical Society has also, by a formal vote, requested this committee to ask for instructions from the larger body, both as to the use of a double standard, and as to the nomenclature and symbols of glucinum or beryllium, and columbium or niobium. With this request we now comply, and hope that every member of the larger International Committee on Atomic Weights will send us his opinion upon the questions thus raised. Shall we continue to issue a double table? Can uniformity in symbols and nomenclature be obtained? And which names are preferable, in the light of history, evidence, and international usage for the two elements under discussion?

That a single standard for atomic weights is most desirable, every chemist will admit; but two standards actually exist, and each one is represented by earnest advocates who are unwilling to give way. Each side of the controversy is supported by eminent authorities in nearly equal numbers, and no agreement seems to be possible either at present or within the near future. This condition of affairs the present committee has been compelled to face, and to deal with things as they are instead of as we should like them to be. Two tables of atomic weight are current and it has therefore seemed wisest to recognize the needs of both parties in the controversy, and to furnish each with trustworthy data for practical use. It is surely better to have one committee prepare both tables, than to leave this work to be done in accordance with individual preferences. That there are difficulties in adjusting one table to the other is perfectly evident, but the resulting confusion is, we think, less serious than some of our critics would have us believe. The confusion is certainly less than it would be, were the individual advocates of either standard to attempt the adjustment of one to the other independently. In short, the real question now

[1] *Chem. News*, **89**, 305.

[2] See reply by F. W. Clarke in *Chem. News*, **90**, 56, July 29, 1904.

before us seems to be this· Shall the present committee act in a quasi-judicial manner, recognizing both parties in controversy, or shall it assume a partisan position and represent one alone?

(Signed).

F. W. CLARKE,
T. E. THORPE,
KARL SEUBERT,
HENRI MOISSAN,
Committee.

INTERNATIONAL ATOMIC WEIGHTS.

		O = 16.	H = 1.
Aluminum	Al	27.1	26.9
Antimony	Sb	120.2	119.3
Argon	A	39.9	39.6
Arsenic	As	75.0	74.4
Barium	Ba	137.4	136.4
Bismuth	Bi	208.5	206.9
Boron	B	11.0	10.9
Bromine	Br	79.96	79.36
Cadmium	Cd	112.4	111.6
Caesium	Cs	132.9	131.9
Calcium	Ca	40.1	39.7
Carbon	C	12.00	11.91
Cerium	Ce	140.25	139.2
Chlorine	Cl	35.45	35.18
Chromium	Cr	52.1	51.7
Cobalt	Co	59.0	58.55
Columbium	Cb	94.	93.3
Copper	Cu	63.6	63.1
Erbium	Er	166.	164.8
Fluorine	F	19.	18.9
Gadolinium	Gd	156.	154.8
Gallium	Ga	70.	69.5
Germanium	Ge	72.5	72.
Glucinum	Gl	9.1	9.03
Gold	Au	197.2	195.7
Helium	He	4.	4.
Hydrogen	H	1.008	1.000
Indium	In	115.	114.1
Iodine	I	126.97	126.01
Iridium	Ir	193.0	191.5
Iron	Fe	55.9	55.5
Krypton	Kr	81.8	81.2
Lanthanum	La	138.9	137.9
Lead	Pb	206.9	205.35
Lithium	Li	7.03	6.98

		O = 16.	H = 1.
Magnesium	Mg	24.36	24.18
Manganese	Mn	55.0	54.6
Mercury	Hg	200.0	198.5
Molybdenum	Mo	96.0	95.3
Neodymium	Nd	143.6	142.5
Neon	Ne	20.	19.9
Nickel	Ni	58.7	58.3
Nitrogen	N	14.04	13.93
Osmium	Os	191.	189.6
Oxygen	O	16.00	15.88
Palladium	Pd	106.5	105.7
Phosphorus	P	31.0	30.77
Platinum	Pt	194.8	193.3
Potassium	K	39.15	38.85
Praseodymium	Pr	140.5	139.4
Radium	Ra	225.	223.3
Rhodium	Rh	103.0	102.2
Rubidium	Rb	85.5	84.9
Ruthenium	Ru	101.7	100.9
Samarium	Sm	150.3	149.2
Scandium	Sc	44.1	43.8
Selenium	Se	79.2	78.6
Silicon	Si	28.4	28.2
Silver	Ag	107.93	107.11
Sodium	Na	23.05	22.88
Strontium	Sr	87.6	86.94
Sulphur	S	32.06	31.82
Tantalum	Ta	183.	181.6
Tellurium	Te	127.6	126.6
Terbium	Tb	160.	158.8
Thallium	Tl	204.1	202.6
Thorium	Th	232.5	230.8
Thulium	Tm	171.	169.7
Tin	Sn	119.0	118.1
Titanium	Ti	48.1	47.7
Tungsten	W	184.	182.6
Uranium	U	238.5	236.7
Vanadium	V	51.2	50.8
Xenon	Xe	128.	127.
Ytterbium	Yb	173.0	171.7
Yttrium	Yt	89.0	88.3
Zinc	Zn	65.4	64.9
Zirconium	Zr	90.6	89.9

Addendum.—Since the foregoing report was written, signed, and sent in for publication, the vote of the larger committee, as solicited by the Committee of the German Chemical Society, has

been received. Fifty-nine members of the larger committee are therein recognized. Thirty-one voted for a table based upon O = 16 exclusively; two for H = 1 exclusively; and five for the simultaneous use of both standards. To the last vote should be added that of the four members of the smaller committee, making nine in all for the double table. Seventeen members refrained from voting. The vote, then, gives one more than a majority of the entire committee in favor of the oxygen standard alone, although the committee appointed by the Chemical Society of Paris in 1900 seems not to have been consulted.

Copies of the report as drawn and agreed to were sent to England, France, Germany, Italy and Japan for simultaneous publication. It is therefore, in the opinion of Professors Thorpe, Seubert, and myself, too late to attempt any change for the current year. To withdraw, rewrite, and re-sign the report would involve too great a delay. We therefore ask for patience on the part of the larger committee, whose wishes will receive due consideration next year.

F. W. CLARKE.

TRIBROMPHENOLBROMIDE: ITS DETECTION, ESTIMATION, RATE OF FORMATION, AND REACTION WITH HYDRIODIC ACID.

BY S. J. LLOYD.

Received October 27, 1904.

THE following experiments form part of an investigation of the reaction between bromine and phenol, which was undertaken with the object of improving Koppeschaar's method of determining the latter substance.

The tribromphenolbromide used was prepared by Werner's[1] recipe, recrystallized three times from chloroform, and dried for three days over sulphuric acid in a vacuum; it formed golden-yellow crystals, melting-point 119°.

DETECTION.

When searching for a distinctive qualitative test for tribromphenolbromide, I found that ammonia, and chloroform solutions of many of the organic bases react with it to form colored products, as follows:

[1] *Bull. Soc. Chim.*, **43**, 372 (1885).

Ammonia	Brown.
Aniline	Deep red, turning muddy.
Dimethylaniline	Slight darkening.
Paratoluidine	Clear red
Diphenylamine	Light red.
α-Naphthylamine	Dark blue, turning purple.
β-Naphthylamine	Light rose-pink, appears very slowly.
Aminoazobenzene	Brown-red, appears very slowly and gradually deepens.
Pyridine	Light yellow.
Benzidine	Intense green, purple if concentrated.

Azoxybenzene, Metanitraniline, Acetanilide, no change.

Of these, aniline and benzidine proved most suitable as reagents; with tribromphenol, tetrabromphenol and hexabromphenoquinone they give no color, while with bromine water an aniline solution is bleached, and benzidine gives a seal-brown, quite distinct from the green with tribromphenolbromide.

The benzidine solution may be prepared by warming 5 grams of benzidine sulphate with 50 cc. of a 10 per cent. potash solution, cooling, extracting the benzidine with chloroform, and filtering off the chloroform solution. Three drops of this reagent give a distinct green with 10 cc. of a solution containing 1 gram of tribromphenolbromide in a liter of chloroform. Shaking the tribromphenolbromide solution with decinormal sodium thiosulphate before adding the benzidine reagent does not interfere with the color reaction.

ESTIMATION.

As the reaction with potassium iodide is obviously unsuitable (see page 20), a basis for the method was sought in the action of reducing agents; Benedict[1] states that zinc and hydrochloric acid reduce tribromphenolbromide to tribromphenol, but does not seem to have made any quantitative measurements. After experimenting with sodium amalgam and with magnesium, I finally decided in favor of powdered zinc and sulphuric acid, which are without action upon tribromphenol, but remove one atom of bromine from tribromphenolbromide. By determining the bromine in the solution after reduction, it is thus possible to calculate the amount of tribromphenolbromide in the substance analyzed. The details of the method are as follows:

The tribromphenolbromide was placed in a 150 cc. flask, 20 cc.

[1] *Ann. Chem.* (Liebig), **199**, 127 (1879).

of alcohol (96 per cent.), 5 cc. N/4 sulphuric acid and about 0.25 gram powdered zinc[1] were added, and the flask heated on a water-bath until the whole of the tribromphenolbromide had dissolved and the solution had lost its characteristic yellow color. Excess of calcium carbonate was then added to neutralize the free sulphuric acid, and the alcohol together with most of the tribromphenol were distilled off on a water-bath; the residue was extracted with three successive portions of boiling water, 25 cc., 25 cc., and 10 cc., respectively; and in the filtrate, after cooling, the bromine was determined by N/10 silver nitrate with potassium chromate as indicator. Blank experiments with tribromphenol showed that no bromine was removed by this treatment.

TEST ANALYSES.

Tribromphenolbromide. Gram.	$AgNO_3$ found. cc.	$AgNO_3$ calc. cc.	Per cent.
0.5023	12.45	12.46	99.92
0.5327	13.19	13.11	100.61
0.5249	12.80	12.92	99.07

NOT THE PRIMARY PRODUCT.

The precipitate formed by the action of bromine water upon phenol is at first pure white in color, but on standing with the solution containing excess of bromine it gradually assumes a yellowish tint; the change is due to the formation of tribromphenolbromide, the presence of which was detected by the qualitative tests described above. The change of color shows that tribromphenolbromide is not the primary product of the action of bromine water upon phenol, as imagined by Weinreb and Bondi,[2] but is formed by a gradual reaction between the precipitated tribromphenol and the excess of bromine.

RATE OF FORMATION.

By means of the method of analysis described above, the amount of tribromphenolbromide formed when the phenol was treated with bromine under varying conditions was determined.

The following solutions were employed: *Phenol*, 20 grams per liter; *silver nitrate*, 16.83 grams per liter; the tribromphenolbromide from 5 cc. of the phenol solution is thus equivalent to 10.74 cc. of the silver nitrate. *Hypobromite*, bromine was dissolved in a solu-

[1] This is more than enough, excess does no harm.

[2] *Monatshefte f. Chemie*, **6**, 506 (1885).

tion of caustic potash of known alkalinity (about quarter normal) and a solution of *hydrochloric acid* equivalent to the potash was prepared, so that on mixing the alkaline solution of bromine with an equal volume of the equivalent acid a neutral bromine solution resulted. By titration with volumetric sodium thiosulphate after adding acid and potassium iodide, 50 cc. of the hypobromite solution were found to contain 0.6810 gram bromine; hence to convert 5 cc. of the phenol solution into tribromphenol requires 37.45 cc. of the hypobromite solution; to convert it into tribromphenolbromide requires 49.94 cc. Allen[1] states that hypobromite solutions prepared like that above, and containing a large excess of alkali do not appreciably alter their content of available bromine upon standing or heating.

The experiments were carried out as follows: 50 cc. of the hypobromite solution were pipetted into a glass-stoppered quarter-liter measuring flask, then 50 cc. of the equivalent acid added and finally 5 cc. of the phenol solution. The mixture was shaken for thirty seconds and allowed to stand for a measured interval, after which the mother-liquor was rapidly removed by means of a filter-pump and a large perforated porcelain funnel. The precipitate was washed with cold water until the addition of silver nitrate produced no cloudiness in the filtrate, and was then brought, filter-paper and all, into a 150 cc. flask, where the tribromphenolbromide was determined as described above.

In some of the experiments the concentration of the bromine was altered by adding bromine from a burette; in others, previous to the addition of phenol, the solution was acidified with hydrochloric acid (sp. gr. 1.2), while in others weighed quantities of potassium bromide were added. The results are contained in Tables I to VI.

The effect of varying the time during which the bromine water acted upon the tribromphenol, *i. e.*, the interval between adding the phenol and filtering, was first studied. The results of these experiments are contained in Table I; they afford ample proof that the tribromphenolbromide is a secondary product and show what a large amount of it may be formed in a few minutes under the ordinary conditions of a phenol determination.

[1] *J. Soc. Chem. Ind.*, **3**, 65 (1884).

TABLE I.—EFFECT OF TIME.

KOBr, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Time. Minutes.	$AgNO_3$. cc.	Tribromphenolbromide. Per cent.
5	2.36	22
10	4.11	38
15	5.13	48
30	7.49	70
Hours.		
18	7.75	72

Under $AgNO_3$ is given the volume of the silver nitrate solution required in the analysis; the numbers under "Tribromphenolbromide" (obtained by dividing the figures in the second column by 10.74) represent the fraction of the phenol which has been converted into tribromphenolbromide.

The experiments of Tables II, III, IV, V and VI show that the amount of tribromphenolbromide formed from 5 cc. of the phenol solution in a constant interval (five minutes) increases with the excess of bromine and with the volume of the reacting mixture, and is diminished by adding acid or potassium bromide, or by lowering the temperature. They afford a striking parallel to the results obtained by Mr. Roebuck in his study of the rate of oxidation of arsenious acid by iodine,[1] where the rate is proportional to the concentration of the iodine and to the volume of the solution, and inversely proportional to the concentration of the acid and of the potassium iodide; Roebuck interpreted his results by assuming that hypoiodous acid is the oxidizing agent in iodine solutions; a similar explanation of my own experiments, *viz.*, that the formation of tribromphenolbromide from tribromphenol is due to the oxidizing action of hypobromous acid, naturally suggests itself.

TABLE II.—EFFECT OF VOLUME.

KOBr, 50 cc.; equiv. HCl, none;* HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Volume. cc.	$AgNO_3$. cc.	Tribromphenolbromide. Per cent.
57	1.19	11
106	2.36	22
157	3.84	36
207	4.6	43

* To keep down the volume. The 1 cc. of strong hydrochloric acid was very slightly more than enough to neutralize the alkali of the hypobromite solution.

[1] *J. Phys. Chem.*, **6**, 365 (1902).

TABLE III.—EFFECT OF BROMINE.

KOBr, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Total excess bromine. Grams.	$AgNO_3$. cc.	Tribromphenolbromide. Per cent.
0.17	2.36	22
0.55	5.59	52
0.92	7.02	66
1.67	8.74	81

TABLE IV.—EFFECT OF ACID.

KOBr, 50 cc.; equiv. HCl, 50 cc.; phenol, 5 cc.

Total acid. Mol.	$AgNO_3$. cc.	Trioromphenolbromide. Per cent.
0.016	2.36	22
0.029	2.78	17
0.068	1.37	13
0.068	1.35	13
0.133	0.35	3
0.198	0.1	1

TABLE V.—EFFECT OF POTASSIUM BROMIDE.

KOBr, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Total KBr. Mol.	$AgNO_3$. cc.	Tribromphenolbromide. Per cent.
0.003	2.36	22
0.0073	1.69	15.7
0.0116	0.51	4.7
0.0288	0.25	2.3
0.0546	0.23	2.2

TABLE VI.—EFFECT OF TEMPERATURE.

KOBr, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Temperature. °C.	$AgNO_3$. cc.	Tribromphenolbromide. Per cent.
0	1.9	18
18	2.36	22

These experiments show clearly that in order to avoid the formation of tribromphenolbromide when titrating phenol with bromine, the liquid must be strongly acid or must contain an excess of potassium bromide; the excess of bromine must not be too great, and the time during which the precipitate of tribromphenol is in contact with the excess of bromine must not be too long. Under these conditions only a mere trace of tribromphenolbromide is formed, and it is precisely when the quantity of that substance is smallest that it is most easily acted upon by hydriodic acid (see Table VII).

REACTION WITH HYDRIODIC ACID.

The statement that tribromphenolbromide reacts with potassium iodide according to the equation

$$C_6H_2Br_3OBr + 2KI = C_6H_2Br_3OK + KBr + I_2$$

is founded on experiments of Weinreb and Bondi.[1] and of Werner.[2] The former obtained 95 per cent. of the theoretical iodine by digesting for twelve hours with an aqueous solution of potassium iodide at 18°, or 99 per cent. at 50°; the latter, using a chloroform solution, obtained 99.96 per cent. The more recent experiments of Kastle,[3] however, show that in chloroform solution, in absence of water, hexabromphenoquinone is the sole product, in which case only half of the iodine called for by the above equation is liberated; while if a carbon bisulphide solution of tribromphenolbromide be treated with an aqueous solution of potassium iodide, the iodine liberated varies from 90 to 100 per cent. of the theoretical amount, depending upon the relative quantities of potassium iodide, water, and carbon bisulphide present. In none of my own experiments, the results of which are detailed in Tables VII and VIII, did I obtain a quantitative yield of iodine; although potassium iodide was present in excess, the acidity of the solution was varied, different solvents were tried, and the digestion was much more prolonged than would be convenient in an analytical method.

It is apparent, however, that as the amount of tribromphenolbromide is reduced, the amount of iodine liberated approaches nearer and nearer to the theoretical value.

TABLE VII.

Expt.	Tribromphenolbromide. Gram.	Solvent.	Time.	*n* HCl. cc.	Iodine. Per cent.	Chloroform or benzene residues.
i	0.2038	none	7 days	..	77	
ii	0.2031	"	7 days	..	78	
iii	0.1747	$CHCl_3$	24 hrs.	..	87	Brown, not green with benzidine.
iv	0.1560	$CHCl_3$	20 hrs.	2.5	91	Deep red with aniline
v	0.1775	$CHCl_3$	8 hrs.	2.5	88	Yellowish red; not green with benzidine.
vi	0.2520	C_6H_6	48 hrs.	..	76	Deep red with aniline.
vii	0.2685	C_6H_6	36 hrs.	5	81	" " " "
viii	0.3045	C_6H_6	24 hrs.	5	84	" " " "
ix	0.2073	C_6H_6	10 min.	5	78	Green with benzidine.

[1] *Monatshefte f. Chem.*, **6**, 506 (1885).
[2] *Bull. Soc. Chim.*, **43**, 373 (1885).
[3] *Am. Chem. J.*, **27**, 31 (1902).

Expt.	Tribromphenolbromide. Gram.	Solvent.	Time.	n HCl. cc.	Iodine. Per cent.	Chloroform or benzene residues.
x	0.2594	C_6H_6	1 hr.	5	80	Green with benzidine.
xi	0.0017	$CHCl_3$	5 min.	5	98	Too dilute.
xii	0.0034	$CHCl_3$	5 min.	5	94	" "
xiii	0.0068	$CHCl_3$	5 min.	5	91	" "
xiv	0.0102	$CHCl_3$	5 min.	5	87	" "
xv	0.0170	$CHCl_3$	5 min.	5	83	" "

In Experiments *i* to *x* the amount taken for analysis was weighed out and placed in a 100 cc. glass-stoppered bottle, the benzene or chloroform (10 cc.) added, then the acid and finally the potassium iodide dissolved in water. In Experiment *v* four times the theoretical amount of potassium iodide was used, in the others twice. The mixture was well shaken and allowed to stand for a measured time, at the end of which the iodine set free was titrated against N/50 thiosulphate. The results of the analyses are entered in the table under "Iodine" as percentages of the amounts of iodine that would have been liberated from the tribromphenolbromide taken had the reaction proceeded according to Werner's equation.

In Experiments *xi* to *xv* a weighed quantity of tribromphenolbromide was dissolved in chloroform, and a measured volume of this solution made up to 10 cc. for each experiment, 5 cc. of normal potassium iodide and 5 cc. of normal acid were added, and the mixture was well shaken and allowed to stand for five minutes, after which the iodine was determined as before.

After completing the analysis, the color of the chloroform or benzene solution was noted, and then a few drops of the aniline or benzidine reagent added. In Experiments *iv*, and *vi* to *x*, the presence of unaltered tribromphenolbromide was established, but in Experiments *iii* and *v*, although the chloroform solutions were colored, no tribromphenolbromide could be detected. This shows that in the experiments in question the deficit of 15 per cent. or so in the iodine is due to the formation of a by-product, and not to the incompleteness of the reaction formulated above. The delicacy of the benzidine test is not sufficient to enable it to be of value in Experiments *xi* to *xv*.

The experiments of Table VIII were carried out in the same way as the first ten of the preceding table, except that the hydrochloric acid was replaced by acetic, and an excess of sodium thiosulphate (5 cc. of a normal solution) was added to the reacting

mixture at the same time as the potassium iodide. The results are very similar to those of Table VII, and show that the deficit is not altogether due to the presence of iodine.

TABLE VIII.

No.	Tribromphenolbromide. Gram.	Solvent.	Time. Hours.	n HAc. cc.	Iodine. Per cent.	Chloroform or benzene residues.
1	0.3195	C_6H_6	24	..	87	No reaction with benzidine.
2	0.1470	C_6H_6	20	5	95.8	" " " "
3	0.1795	C_6H_6	18	5	95.6	" " " "
4	0.2145	C_6H_6	24	5	92.1	" " " "
5	0.2748	$CHCl_3$	24	5	93.3	" " " "

From these experiments it is apparent that if in a phenol determination part of the tribromphenol precipitate is converted into tribromphenolbromide, the latter will not be quantitatively transformed into tribromphenol by the action of potassium iodide, and an error will thus be introduced into the analysis.

SUMMARY.

(1) Aniline and benzidine may be used as qualitative reagents for tribromphenolbromide.

(2) Tribromphenolbromide is quantitatively reduced to tribromphenol by zinc and sulphuric acid; a convenient method for its determination, based on this reaction, is described.

(3) Tribromphenolbromide is not a primary product of the action of bromine on phenol, but is formed by the gradual action of bromine water on tribromphenol. As the rate of this reaction is decreased by adding acid or potassium bromide, and increased by adding water or bromine (or by raising the temperature), it is probably due to the presence of hypobromous acid in the bromine water.

(4) Tribromphenolbromide is not quantitatively reduced to tribromphenol by hydriodic acid under conditions convenient for analysis; this is due in part to the formation of other products.

My thanks are due to Prof. W. Lash Miller, at whose suggestion this research was undertaken and under whose supervision it has been carried out.

THE UNIVERSITY OF TORONTO,
June, 1904.

THE DETERMINATION OF PHENOL.

By S. J. Lloyd.

Received October 27, 1904.

Numerous attempts have been made to devise a satisfactory method for the quantitative estimation of phenol.

Beckurts[1] mixed the phenol with its own volume of petroleum spirit, shook with a strong solution of caustic soda in a graduated tube, and noted the change in volume; Bader[2] titrated against a decinormal solution of sodium hydroxide with symmetrical trinitrobenzene as indicator;[3] Messinger and Vortmann[4] precipitated the triiodo derivative with an alkaline solution of iodine; Carré[5] treated the phenol with nitric acid and determined the resulting picric acid colorimetrically; Schaedler[6] used sulphuric acid, and determined the phenolsulphonic acid indirectly with barium; Riegler[7] weighed the precipitate with *p*-diazonitraniline; Toscher[8] oxidized with volumetric permanganate in boiling alkaline solution; while the reaction with sodamide has been applied by Schryver[9] to the determination of the "hydroxyl value" of phenol.

Of these methods, the first evidently makes no pretense to accuracy, and indeed, like the sulphonic acid process, is intended for use with crude phenol only. Titration with soda is not possible with solutions containing less than 2 per cent. of phenol,[10] and in any case the end-point is not sharp. Precipitation with iodine requires careful manipulation and exact regulation of the temperature in order to obtain accurate results;[11] the colorimetric method is unsuited to the determination of phenol in other than very small quantities, the reaction with the diazo compound leads to a tedious gravimetric process, and the sodamide method requires special apparatus, and can be used only with perfectly dry phenol.

The reaction of phenol, however, which is best suited for the

[1] *J. Soc. Chem. Ind.*, **5**, 546 (1886) (from *Arch. Pharm.*, **24**, 567 (1886)).

[2] *Ztschr. anal. Chem.*, **31**, 58 (1892).

[3] For the behavior of phenol with other indicators, see Imbert and Astruc: *Compt. Rend.*, **130**, 35 (1900).

[4] *Pharm. Ztg.*, **29**, 759.

[5] *Compt. Rend.*, **113**, 139 (1891).

[6] *Centrbl.*, 1872, p. 506 (from *Pharm. Centrbl.*, **13**, 225).

[7] *Centrbl.*, 1899, II, p. 322 (from *Buletinul din Bucuresci*).

[8] Meyer's *Jahrbuch, d. Chemie*, 1901, p. 253 (from *Pharm. J.*, 1901, No. 1602).

[9] *J. Soc. Chem. Ind.*, **18**, 553 (1899).

[10] Frerichs: *Centrbl.*, 1896, II, p. 2141 (from *Apoth. Ztg.*, **11**, 415).

[11] Frerichs: *Loc. cit.*

purposes of quantitative determination, is that with bromine,

$$C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr.$$

Landolt,[1] who was the first to suggest its use, precipitated the tribromphenol with bromine water, dried in a desiccator and weighed; Chabrie[2] extracted with ether and dried in a special apparatus. Koppeschaar[3] shortened the process by using a measured quantity of bromine water, and titrating back the excess with potassium iodide and sodium thiosulphate; he also found it advisable to replace the unstable and disagreeable bromine water by a mixture of potassium bromide and bromate, from which the bromine was liberated at the proper time by acid. Degener,[4] who was apparently unacquainted with Koppeschaar's work, also used bromine water, but determined the end-point by the disappearance of the yellow color of the solution, or by potassium-iodide-starch paper. Chandelon[5] found the time required for an analysis by the Koppeschaar method too long, and in order to shorten it and avoid loss of bromine as vapor and as a mechanical enclosure in the precipitate, he substituted for the bromide-bromate mixture a hypobromite solution which contained sufficient alkali to hold the tribromphenol in solution. The disappearance of the yellow color of the solution, or the failure to discolor potassium-iodide-starch paper, marked the end of the reaction. Telle[6] used volumetric sodium hypochlorite, which he added to the solution of phenol containing excess of potassium bromide, and determined the end-point by the color of the solution. Waller's[7] method differed from that of Degener only in the addition of a saturated solution of alum to make the precipitate more dense. Seubert[8] followed Koppeschaar in liberating the bromine from a bromide-bromate mixture, and added the phenol solution from a burette until the filtrate gave no further color with potassium-iodide-starch paper, while Beckurts[9] used an excess of the bromide-bromate mixture, and titrated back with iodide and thiosulphate. The last-named chemist recognized the presence of tribromphenolbromide

[1] *Ber. d. chem. Ges.*, **4**, 770 (1871).
[2] *Centrbl.*, 1898, **1**, 1309 (from *Rev. Chim. Anal. Appl.*, **6**, 138 (1898)).
[3] *Ztschr. anal. Chem.*, **15**, 233 (1876).
[4] *J. prakt. Chem.*, N. F., **17**, 390 (1878).
[5] *Bull. Soc. Chim.*, **38**, 69 (1882).
[6] *Chem. News.*, **83**, 51 (1901).
[7] *Ibid.*, **43**, 152 (1881).
[8] *Ber. d. chem. Ges.*, **14**, 1581 (1881), (from *Arch. Pharm.*, **15**, 321).
[9] *J. Soc. Chem. Ind.*, **5**, 546 (1886) (from *Arch. Pharm.*, **24**, 561 (1886)).

in the precipitate, but assumed that it was quantitatively converted into tribromphenol by potassium iodide.

The following table may serve as a synopsis:

Gravimetric:

(1) Landolt, Chabrié.

Volumetric:

(2) *Bromine and phenol in acid solution.*

(*a*) End-point determined by color, or by potassium-iodide-starch paper.

Degener—Bromine water.
Telle —Hypochlorite and potassium bromide.
Waller —Bromine water and alum.
Seubert —Bromide-bromate mixture.

(*b*) Excess bromine determined by potassium iodide.

Koppeschaar—Bromine water or bromide-bromate mixture.
Beckurts—Bromide-bromate mixture.

(3) *Bromine and phenol in alkaline solution.*

Chandelon.

Various modifications for use in the estimation of phenol in tar-oil, urine, soaps, etc., have been suggested by Tóth,[1] Kleinert,[2] Fedeli,[3] Giacosa,[4] Endemann, Neuberg,[5] Kossler and Penny,[6] Partheil,[7] Ditz and Cedivoda,[8] Stockmeier and Thurnauer[9] (who used chloroform in the titration), and others.

Some idea of the accuracy of the results obtainable by these different methods of procedure may be gleaned from the test analyses published by their authors. Landolt's numbers show variations of 0.5 per cent. or more. Koppeschaar's (bromine water) 2.5 per cent. (bromide-bromate) 0.5 per cent., Degener's 3 per cent., Chandelon 2 per cent., Seubert's 1.5 to 3 per cent. No test analyses have been published by Waller or Telle. According to Frerichs,[10] Beckurt's modification is the best, but as his paper, in its original form, is not accessible to me, I am unable to quote the results of this author's analyses.

These discrepancies are due, in part at least, to the formation

[1] *Ztschr. anal. Chem.*, **25**, 160 (1886).
[2] *Ibid.*, **23**, 1 (1884).
[3] *Ber. d. chem. Ges.*, **28**, 1060 R (1895), (from Moleschott's *Untersuchung.*, **15**, 585).
[4] *Ztschr. physiol. Chem.*, **6**, 43 (1878).
[5] *Ibid.*, **27**, 123 (1899).
[6] *Ibid.*, **17**, 117 (1889).
[7] Meyer's *Jahrbuch d. Chemie*, 1896, p. 237 (from *Apoth. Ztg.*, 1896).
[8] *Ztschr. angew. Chem.*, 1899, pp. 873 and 897.
[9] Mohr: *Titrirmethode*, 7th ed., p. 386 (1896) from *Chem. Ztg.*, 1893, pp. 119 and 151.
[10] *Centrbl.*, 1896 (II), 2141.

of tribromphenolbromide, which, as I have shown in a previous paper,[1] is produced by the action of bromine water on the precipitated tribromphenol, and once formed is not quantitatively reconverted into tribromphenol by potassium iodide.

The present paper, after dealing with the loss of bromine by evaporation during the analysis, the use of volumetric solutions containing bromates, and the formation of a new product of the action of bromine on phenol, contains the results of a number of test-analyses in which the precautions suggested by the previous experiments were adopted, and closes with an enumeration of the conditions under which phenol may be accurately determined.

SOLUTIONS EMPLOYED.

Phenol.—Merck's "absolute phenol" was distilled three times, the first and last fractions being rejected in each case, and the portions boiling between 182° and 183° collected. In the last fractionation the distillate was received in a tared and stoppered weighing-glass, cooled, weighed (20.5340 grams) and dissolved to 1 liter. The solution used in the following analyses was made by diluting 100 cc. of this solution to 1 liter.

Hypobromite.—About 9 cc. of bromine were dissolved in 2 liters of N/4 caustic potash, and the solution was standardized by adding potassium iodide and hydrochloric acid, and determining the iodine with decinormal thiosulphate.

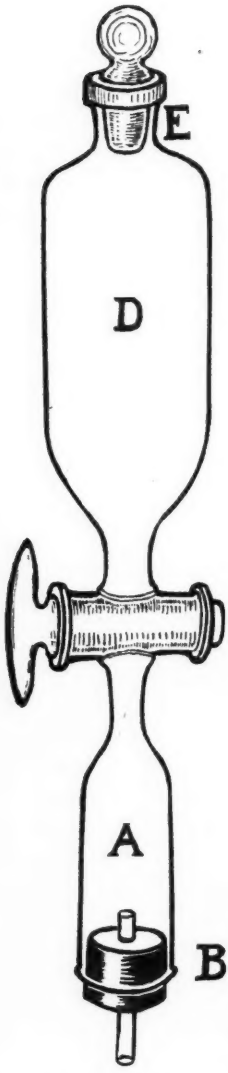
One hundred cc. of the phenol solution were equivalent to 71.95 cc. of the hypobromite.

Sodium Thiosulphate.—One liter of an approximately N/10 solution was prepared and standardized with iodine which had been ground with potassium iodide, sublimed from the mixture, and dried for three days in a vacuum desiccator over sulphuric acid. The value was found to be 0.1045 N. This solution was used to fix the titre of the alkaline solution of bromine as stated above, and in turn was repeatedly standardized against the latter solution; it showed a slight falling off in normality from 0.1045 to 0.1042 in two weeks.

For use in the phenol determination the decinormal thiosulphate was diluted to five times its volume and the ratio controlled by comparison with an iodine solution.

Iodine, approximately N/50 for use in "titrating back."

[1] This Journal, **27**, 7 (1905).



Acid, hydrochloric, "strictly chemically pure" (sp. gr. 1.2).

Potassium Iodide, 17 grams in 100 cc.

The solutions were prepared and standardized with every care, the burettes were calibrated before using, and a special burette reader was employed, by means of which hundredths of a cubic centimeter could readily be distinguished.

LOSS OF BROMINE BY EVAPORATION.

The test analyses published at the close of this paper were carried out in a 0.25 liter long-necked glass-stoppered measuring flask. In order to assure myself that there was no loss of bromine by evaporation, two measurements were made in the apparatus sketched in the accompanying figure (made by sealing an adapter to a separating funnel).

The chamber *A* was closed by the perforated rubber stopper *B*, the tap opened and the whole exhausted with a filter-pump; the tap was then closed, *B* removed, and the apparatus fixed in a stand, *A* upwards. Fourteen cc. of the hypobromite (or bromide-bromate solution) were then pipetted into *A* and sucked into *D* by slightly opening the tap; this was followed by 25 cc. of acid and then 20 cc. of phenol solution; the vessel *A* was rinsed out with 10 cc. of water between each addition and the rinsings sucked into *D*. After shaking and allowing to stand for five minutes, 5 cc. of the potassium iodide solution were added in the same manner; the tap was then opened to restore atmospheric pressure in *D* and the contents poured through *E* into a beaker containing 150 cc. of water, where

the iodine was titrated by sodium thiosulphate. From the thiosulphate required the excess of bromine was calculated, and by subtracting from the original 14 cc. the "KOBr used" of the table was obtained.

Experiments identical in every respect, except that the 250 cc. flask was used instead of the apparatus just described, were carried out at the same time; as is shown in Table I, the results differ only by one or two parts per thousand. It is thus proved that the operation may be carried out in a flask without loss of bromine. Some care, however, is necessary; in one case where the bromine vapor was purposely blown out of the flask, an error of 2 per cent. in the analysis resulted.

TABLE I.

Hypobromite, 14 cc.; acid, 25 cc.; water, 30 cc.; phenol, 20 cc.; iodide, 5 cc.; time, five minutes.

Hypobromite.	Apparatus.	KOBr used.	Differences.
Fresh	Flask	13.91	0.0
Fresh	See figure	13.91	
Evaporated	Flask	13.96	0.02
Evaporated	See figure	13.94	

ACTION OF BROMIC ACID ON PHENOL AND THE USE OF THE BROMIDE-BROMATE MIXTURE.

If a little potassium bromate be mixed with a solution of phenol and acid be added, the solution turns red and a red precipitate is deposited which contains bromine and does not liberate iodine with hydriodic acid. It is obvious that the formation of this substance, during the determination of phenol, would vitiate the result.

As old solutions of potassium hypobromite are liable to contain bromate, two pairs of experiments were undertaken to see whether errors could be introduced into the analysis from this source; in one of each pair 14 cc. of fresh hypobromite solution were used and in the other a solution of bromide and bromate made by evaporating 14 cc. of the same hypobromite to dryness and dissolving the residue. In one experiment of each of the pairs the reagents were mixed in the order *A*, hypobromite (or bromide-bromate mixture), acid, phenol, and in the other in the order *B*, acid, phenol, hypobromite (or bromide-bromate). The results with the bromide-bromate mixture were 3 or 4 parts per thousand higher than the others, while the order of mixing made no difference (see Table II). It is thus clear that the presence of a little bromate

in the hypobromite solution can exert no influence whatever on the result.

TABLE II.

Hypobromite, 14 cc.; acid, 25 cc; water, 30 cc.; phenol, 20 cc.; iodide, 5 cc.; time, five minutes.

Hypobromite.	Order of mixing.	KOBr used.
Fresh	*A*	13.91
Fresh	*B*	13.94
Evaporated	*A*	13.96
Evaporated	*B*	13.96

NEW PRODUCT OF THE ACTION OF BROMINE ON PHENOL.

If solutions of phenol and potassium hypobromite be mixed and the mixture be acidified, the precipitated tribromphenol is mixed with a red powder. What seems to be the same compound was obtained as a by-product in the preparation of tribromphenolbromide, and by the action of alkaline solutions of bromine on tribromphenol. It melts at about 91° C. and contains about 64 per cent. of bromine, but does not liberate iodine with an acid solution of potassium iodide. It is insoluble in water, alcohol, ether, and in glacial acetic acid; soluble in carbon bisulphide, chloroform and benzene, giving red solutions. Its molecular weight in chloroform solution (boiling-point determinations) is 508 to 514. On warming with a 10 per cent solution of caustic potash, or with concentrated sulphuric acid, it is apparently unaltered, but by heating to a temperature above its melting-point it is converted into a substance resembling hexabromphenoquinone.

I propose, if possible, to determine the constitution of this substance. Its formation during an analysis would, obviously, introduce errors into the result, hence the analytical method of group 3 (page 18) cannot be recommended.

THE DETERMINATION OF PHENOL.

Four of the most likely sources of error in the present methods of determining phenol by bromine having been studied in detail, it remained to inquire whether determinations carried out under the conditions suggested by the foregoing experiments, would give accurate results. The test-analyses undertaken with the object of deciding this question were made in acid solution in order to avoid the formation of tribromphenolbromide;[1] they were carried out at room temperature in a long-necked, glass-stoppered 0.25-liter flask (page 20), and the bromine was introduced in the convenient form of a solution in caustic potash (page 22). The

[1] This Journal, **27**, 7 (1905).

phenol solution was run into the flask from a burette, the acid added, and then the hypobromite from a pipette. The flask was closed, shaken for thirty seconds, and allowed to stand for the time given in the table after "t." Five cc. of potassium iodide solution were then added, followed by 100 cc. of water, and in some cases 10 cc. of chloroform. The whole was shaken for fifteen seconds, allowed to stand for two minutes, and the iodine determined with the N/50 thiosulphate.

TABLE III.

Hypobromite, 25 cc.; acid, 15 cc.

		10 cc. chloroform.		No chloroform.		
Phenol. cc.	Excess Br. cc.	$t = 0$. Per cent.	$t = 2$ minutes. Per cent.	$t = 0$. Per cent.	$t = 2$ minutes. Per cent.	$t = 5$ minutes. Per cent.
5	21.40	....	114.0	105.6	105.6	106.2
10	17.80	....	109.6	103.9	103.7	103.9
15	14.21	....	100.10	....	....	....
20	10.61	100.0	99.95	....	99.97	100.11
20	10.61	....	....	....	101.51*	102.71*
20	10.61	....	....	....	....	101.92†
25	7.01	....	100.05	99.62	99.83	99.83
25	7.01	....	....	....	100.35*	....
25	7.01	....	....	....	99.85	....
30	3.42	99.9	99.95	99.56	97.7	99.83
30	3.42	....	....	99.6	99.65	99.85
31	2.70	99.8	99.8	99.44	99.55	99.97
32	1.98	....	99.85	99.25	99.35	99.97
33	1.26	....	98.99	98.7	99.35	99.7
34	0.54	....	98.62	98.1	98.9	99.42
35	0.18	....	97.63	96.9	....	98.74

Under "Excess Br" is given the difference between the volume of the hypobromite employed, *viz.*, 25 cc. and the volume equivalent to the phenol taken (volume of phenol solution multiplied by 0.7195, see page 19). The results of the determinations are expressed as percentages of the amount of phenol actually present.

In the experiments marked with a star (*), 10 cc. of carbon bisulphide were used instead of chloroform, and in that marked dagger (†), 5 cc. of acid were used instead of 15 cc. In this experiment the precipitate, dissolved in chloroform, gave a distinct green with benzidine solution, indicating the presence of tribromphenolbromide.

Table IV contains the results of a few measurements in which sulphuric acid was used instead of hydrochloric. It is obvious that Koppeschaar[1] was mistaken in saying that the presence of sulphuric acid spoils the titration.

[1] *Ztschr. anal. Chem.*, **15**, 237 and 240.

TABLE IV.

Hypobromite, 25 cc.; sulphuric acid (sp. gr. 1.84), 11 cc.; chloroform, 10 cc.

Phenol. cc.	Excess Br. cc.	$t = 2$. Per cent.
20	10.61	99.91
25	7.01	99.85
30	3.42	100.11

The above experiments lead to the following:

DIRECTIONS FOR THE DETERMINATION OF PHENOL BY BROMINE.

The following solutions are needed.—Fiftieth-normal thiosulphate and iodine; starch; hydrochloric acid (sp. gr. 1.2); potassium iodide, 17 grams in 100 cc.; hyprobromite, prepared by dissolving 9 cc. of bromine in 2 liters of a solution containing 28 grams of caustic potash. The hypobromite must be compared with the thiosulphate by adding acid and potassium iodide and titrating the iodine set free.

To carry out the analysis.—Introduce the phenol solution into a glass-stoppered flask and add a volume of acid equal to about one-third or one-fourth of the combined volumes of the phenol solution and the hypobromite that will probably be added during the analysis.

Run in the hypobromite from a burette, shaking the flask, until the solution becomes permanently yellow. Then add an excess of the hypobromite (10 to 20 per cent. of that used already) and shake well. Finally add an excess of potassium iodide, dilute with water, add 10 cc. of chloroform, and determine the iodine with the volumetric thiosulphate. The object of diluting is to prevent the acid from acting on the potassium iodide or on the thiosulphate; if 10 cc. of water be added at this stage for every cubic centimeter of acid previously added, the solution will be sufficiently dilute. The use of chloroform may be dispensed with, if the mixture be allowed to stand five minutes before adding the potassium iodide; it is, however, better to use the chloroform,—carbon bisulphide is not satisfactory.

If these directions be adhered to, the phenol can be determined within 1 or 2 parts per thousand.

In conclusion, the author wishes to express his thanks to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose direction it has been carried out.

THE UNIVERSITY OF TORONTO,
March, 1904.

[Contribution from the Food Division of the Bureau of Chemistry, U. S. Department of Agriculture, No. 56.
Sent by H. W. Wiley.]

A NOTE ON THE DETECTION OF ARCHIL, CUDBEAR, AND OTHER LICHEN COLORS.

By L. M. Tolman.

Received October 22, 1904.

Archil, orseille or orchil, as it is variously called, and cudbear, coloring materials produced from lichens, are being used to a considerable extent for coloring medicines and foods where colors of coal-tar origin are prohibited.

The methods of analysis now employed to detect coal-tar dyes are liable to lead the analyst to an erroneous decision in the presence of these lichen colors, and it is for this reason that this note is written. The methods most often employed for the detection of coal-tar colors in foods and medicines are those of Sostegni and Carpentieri and Arata, as given in the "Provisional Methods for the Analysis of Foods."[1] These depend on the dyeing of wool in an acid-bath, then extracting the color with ammonia, acidifying this solution and dyeing a second piece of wool.

This process eliminates the natural colors of the fruits and wines and collects the coal-tar color on the wool where it can be tested with various reagents. If, however, lichen colors, such as archil are present, they will be mistaken for coal-tar dyes, if these tests alone are used, as these colors dye wool readily in acid-bath, and are extracted by dilute ammonia, and on making this solution acid again, wool will be readily dyed. It is necessary, after having applied these dyeing tests, to make further tests before deciding that the dye present is of coal-tar origin.

It is, however, comparatively easy to distinguish the lichen colors from those of coal-tar origin.

These colors can be extracted from ammoniacal solution by amyl alcohol, which separates them from the natural colors of the fruits and wines.[2] This amyl alcohol extract, of a purplish red color, is evaporated on the steam-bath to drive off the amyl alcohol, and the purified color tested.

[1] U. S. Department of Agriculture, Bureau of Chemistry, Bull. 65, pp. 111 and 112.
[2] *Ibid.*, p. 113.

A water solution of this color is readily reduced by tin and hydrochloric acid, and reoxidized by ferric chloride. This at once eliminates all the azo dyes and magenta, which are by far the most common dyes used, and leaves only dyes of Class II of the scheme proposed by Rota.[1] All the coal-tar dyes used as archil substitutes and which resemble it in color are azo dyes, and can be readily distinguished from the archil color. If it is desired still farther to identify the color, it can be treated as described by Allen.[2] If it is found by the wool dyeing tests that some added color is present and that amyl alcohol extracts a reddish purple color from an ammoniacal solution, which is readily reduced by tin and hydrochloric acid and reoxidized by ferric chloride, we may be certain that the color is one of the lichen colors, archil, cudbear or litmus, all of which act in a similar way.

These colors are on the market in a number of different forms, as extracts or pastes, as ground-up lichens, or as sulphonated orceïne. This latter form might be readily mistaken for a coal-tar dye on account of its appearance and solubility, but it gives all the reactions of the non-sulphonated colors and can be identified as described above.

THE BASIC PROPERTIES AND THE QUADRIVALENCE OF OXYGEN.

By D. McINTOSH.

Received October 18, 1904.

IN A paper[3] on the basic properties of oxygen, Archibald and McIntosh, continuing the work on the chemistry of low temperatures begun by Walker, McIntosh and Archibald[4] have described additive compounds of organic substances containing oxygen with the halide acids, and have shown that the constitutions of these compounds can be satisfactorily represented by assuming oxygen to have a valency higher than two. Such a supposition was almost imperative in the case of the compounds investigated containing only hydrogen, carbon and oxygen, since

[1] *Chem. Ztg.*, **22**, 437-442; 1898, U. S. Department of Agriculture, Bureau of Chemistry, Bull. 65, pp. 115-118.

[2] Vol. III, part 1, pp. 525 to 541.

[3] *J. Chem. Soc.* (London), **85**, 919 (1904).

[4] *Ibid.*, **85**, 1098 (1904).

hydrogen is looked upon as a monad, and experiments have as yet failed to show the existence of substances in which the valency of carbon exceeds four.

In some of the compounds described, such as those formed from liquefied hydrochloric acid and the ethers, the valency of the oxygen might even be assumed to be as high as twelve. But since hydrogen choride in contrast to hydrogen bromide and iodide polymerizes when liquefied, the valency of the chlorine might with equal justice be looked upon as rising from one to three, while the oxygen remains quadrivalent.

Archibald and McIntosh's collected results appear in the following table and indicate that as the temperature at which these bodies are stable decreases, the valency of the oxygen increases, but only in the case of the hydrogen chloride compounds is it greater than six. This result is of sufficient interest to warrant the investigation of a few more compounds of hydrogen iodide and bromide which seem likely to melt at a low temperature, and thus to show whether oxygen can exist under these conditions, with a valency of eight or twelve.

	Molecules of acid.	Molecules of organic liquid.	Melting-point.	Valency of oxygen.
HI	1	Acetone (2)	— 18°	4
	1	Ether (1)	— 18	4
	2	Propyl alcohol (1)	— 70	6
HBr	1	Acetone (1)	— 9	4
	1	Ether (1)	— 40	4
	2	Propyl alcohol (1)	— 85	6
HCl	5	Acetone (2)	— 85	8
	5	Ethyl ether (1)	— 92	12
	5	Methyl ether (1)	—120(?)	12
	5	Propyl alcohol (1)	—120(?)	12

Of the ethers, the most likely for the purpose mentioned above was the most volatile one of the fatty series, dimethyl ether, boiling at —26° C.; an ether, too, of particular interest, on account of the work of Friedel, who predicted the influence of temperature on valency, and who was the pioneer in what may be called low temperature chemistry. The other body containing oxygen chosen as the most suitable was methyl alcohol.

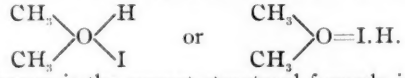
The methods of preparation of the halogen acids and of the compounds are described in the paper previously referred to. The

compounds were white, crystalline, almost insoluble[1] in the ether or alcohol, but quite soluble in the acid from which they were made, and in which they readily formed supersaturated solutions from which they could be precipitated by the addition of the solid phase. They had a sharp melting-point and their formation took place with the evolution of a large amount of heat.

The method of analysis was similar to that previously described. The body was dried in a jacketed filter-tube by means of air drawn through it, and it may be well to point out that the amount of acid found in such a compound will be invariably low. Indeed, it seems hardly possible to devise a method which will give results neither too low nor too high; for if the alcohol or ether is used to wash the body, some will be absorbed and the results will be low; if acid is used, it will be in excess and the results will be high. The alcohol or ether has, in all cases, been used for washing.

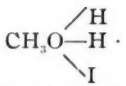
1. The compound of methyl ether and hydriodic acid melted at —15° C. The following are the results of the analyses (Preparation I was washed with a comparatively large amount of ether; Preparation II with very little): Preparation I gave 65.9, 66.9, 66.4; mean, 66.4 per cent. hydriodic acid. Preparation II gave 68.3, 69.6, 70.0; mean, 69.3 per cent. C_2H_6OHI requires 73.6 per cent. of acid, while $(C_2H_6O)_2HI$ requires 58.2 per cent.

The formula is therefore $C_2H_6O.HI$, and the constitution



That the former is the correct structural formula is almost certain, for in the case of diethyl ether dissolved in a halide acid, Dr. Steele[2] has shown that the ether moves to the cathode during electrolysis.

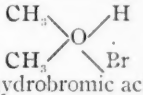
2. Methyl alcohol and hydriodic acid gave a compound melting at —48°. The analytical results are: I, 76.0, 78.4; II, 76.2, 75.6; mean, 76.5 per cent. hydriodic acid. CH_4OHI requires 80 per cent. acid. The constitution is therefore



[1] While water is quite insoluble in either the halogen acid or the ether at low temperature, it is apparently much more soluble in some mixtures of the two.

[2] The account of this work is as yet unpublished, but Dr. Steele has kindly allowed me to make use of this result.

3. Methyl ether and hydrobromic acid. Melting-point, —22°. The analysis gave: I, 63.2, 64.2, 63.3; mean, 63.6. II, 63.2, 63.6, 63.3; mean, 63.3 per cent. hydrobromic acid. C_2H_6OHBr requires 63.8 per cent. of acid, and the constitution is therefore



4. Methyl alcohol and hydrobromic acid. Melting-point, —14°. The analysis gave: I, 67.8; II, 68.5, 68.6; mean, 68.3 per cent. hydrobromic acid. CH_4OHBr requires 71.7 per cent. of acid and the constitution is

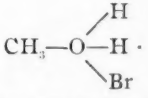


TABLE II.—COLLECTED RESULTS.

	Molecules of acid.	Molecules of organic liquid.	Melting-point.	Valency of oxygen.
HI	1	Ether (1)	—15°	4
	1	Alcohol (1)	—48	4
HBr	1	Ether (1)	— 22	4
	1	Alcohol (1)	—14	4

In the above table the analytical results are collected and show the simplest proportion in which the bodies are formed and the temperatures at which they decompose (melt). The low melting-point of the compounds of alcohol with hydrogen iodide, as compared with the corresponding hydrogen bromide compound, is strange, but a similar anomaly was noticed with acetone (Table I). The oxygen is in all cases quadrivalent and from a comparison of the melting-points with those in Table I this is to be expected.

These compounds, therefore, are unsuitable for the purpose for which the research was undertaken and I can think of no bodies containing oxygen, which with hydrogen iodide[1] or bromide seem likely to give additive compounds melting at —90° or —100°. We must then, for the present, regard six as the highest valency of oxygen, a number which agrees perfectly with its position in the sixth column of the periodic table.

MACDONALD CHEMICAL LABORATORIES,
McGILL UNIVERSITY, MONTREAL,
October, 1904.

[1] Other acids give additive compounds with organic bodies. With sulphuric acid: see Hoogewerff and W. A. Van Dorp, *Recueil. trav. chim. Pays-Bas*, **21**, 349 (1902); nitric acid probably acts like sulphuric, while chlorsulphonic acid gives a series of stable bodies with the ethers.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

A STUDY OF THE MERCURY SULPHOCYANATE COMPLEXES.

BY M. S. SHERRILL AND S. SKOWRONSKI.

Received November 18, 1904.

I. INTRODUCTION.

ANY theory of valence to be fully satisfactory must be capable of explaining the existence of at least all complex compounds which are stable enough to exist either in solution or the gaseous state. From a valence standpoint, therefore, a study of such complexes and a determination of their molecular formulas is very important.

Moreover, an interesting relation between the tendency of the elements to form complexes and their position in the electrochemical series has been pointed out by Abegg and Bodländer.[1] This principle states that the tendency towards complex formation increases with decreasing electro-affinity, of which the decomposition-potential may be taken as a measure. The stability of a complex is a measure of the tendency of its constituents to combine, and is greater the smaller the amount of the complex which is dissociated into its component ions. It may be expressed mathematically in the form of a constant, called by Bodländer[2] the *stability constant,* which is equal to the concentration of the complex divided by the product of the concentrations of the component ions raised to that power which, according to the law of mass action, corresponds to the number of single ions constituting the complex.

To compare quantitatively the tendency of the halogens to form complexes, a study of the complexes formed by dissolving the mercuric halides in a solution containing a common anion is especially suitable. As has been established by many kinds of observations, this solution takes place with the formation of a complex anion according to the general reaction,

$$m\mathrm{HgX_2} + n\mathrm{X^-} \rightleftarrows (\mathrm{HgX_2})_m(\mathrm{X^-})_n .$$

The more stable this complex is, the less will it be decomposed into its single ions according to the reactions,

[1] *Ztschr. anorg. Chem.*, **20**, 472 (1899).

[2] *Ber. d. chem. Ges.*, **36**, 3935 (1903).

$$(HgX_2)_m(X^-)_n \rightleftarrows mHg^{++} + (2m + n)X^-,$$

and the larger will be its stability-constant,

$$K_1 = \frac{[(HgX_2)_m(X^-)_n]}{[Hg^{++}]^m[X^-]^{2m+n}}.$$

According to the principle of Abegg and Bodländer stated above, the value of this constant should increase in the series, $HgCl_2$, $HgBr_2$, HgI_2, $Hg(CN)_2$, in the order named. One of us[1] has studied the complex formation and determined the stability constants of these four salts. It was the purpose of this work to extend this investigation to mercuric sulphocyanate.

II. SOLUBILITY OF MERCURIC SULPHOCYANATE IN POTASSIUM SULPHOCYANATE SOLUTIONS.

One method of determining the formula of the complex is to measure the solubility of mercuric sulphocyanate in varying strengths of potassium sulphocyanate solution; for the increase of solubility over that in pure water is a quantitative measure of the complex formation as represented by the general equation,

$$mHg(SCN)_2 + nSCN^- \rightleftarrows (Hg(SCN)_2)_m(SCN^-)_n. \qquad (1)$$

From this equation and the law of mass action it follows that

$$\frac{[(Hg(SCN)_2)_m(SCN^-)_n]}{[Hg(SCN)_2]^m[(SCN^-)]^n} = K_2. \qquad (2)$$

Here, as well as in the following discussions, we will let a represent the original concentration of the potassium sulphocyanate solution, b the concentration of the free mercuric sulphocyanate existing as such in the solution, and c that of the mercuric sulphocyanate present in the complex. It follows then from equations (1) and (2) that

$$K_2 = \frac{\frac{c}{m}}{b^m\left(a - \frac{n}{m}c\right)^n}. \qquad (3)$$

Complete dissociation of the potassium sulphocyanate and of the complex salt into the corresponding ions is here, as in subsequent considerations, assumed. Although this assumption is certainly not exact, it cannot affect the order of magnitude of the constants.

Since in these solubility experiments mercuric sulphocyanate is

[1] *Ztschr. phys. Chem.*, **43**, 705 (1903).

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present as a solid phase, the concentration b of the free mercuric sulphocyanate in the solution must be constant and equal to its solubility in water. The concentration c of the mercuric sulphocyanate bound as complex in the solution is equal to its total concentration or total solubility diminished by the concentration of the part uncombined, b.

The values of a, b and c being now known, to determine the formula of the complex, it would seem only necessary to make such assumptions as to m and n as would make the expression remain constant. It is, however, to be borne in mind that in saturated solutions, the concentration of the SCN^- ion, owing to its disappearance in the form of the complex is very small, and that therefore a small error in the determination of c will cause a large error in $\left(a-\frac{n}{m}c\right)$, and since this term is raised to the nth power it will render the whole expression uncertain. For this reason exact values for m and n cannot be determined by such solubility experiments. When, however, the concentration of the SCN^- ion is negligibly small, the ratio $\frac{a}{c}$ must approximate to $\frac{n}{m}$; for in case all of the SCN^- ions disappear in the form of the complex according to equation (1), $\frac{a}{c}$ must become equal to $\frac{n}{m}$. For this same reason Jander,[1] who has measured the solubility of mercuric sulphocyanate in potassium sulphocyanate solutions, was not justified in concluding that n is equal to 1 from the fact that the ratio $\frac{a}{c}$ remains constant.

The solubility experiments were made by rotating potassium sulphocyanate solutions of various concentrations in a thermostat at 25° for several hours with an excess of mercuric sulphocyanate, which had been purified by crystallizing twice from hot water. The exact concentration of the potassium sulphocyanate solutions was obtained by titrating them with a silver nitrate solution of known strength with ferric alum as an indicator. After settling, samples were pipetted off, and the mercuric salt dissolved was determined by precipitating with hydrogen sulphide and weighing the mercuric sulphide in a Gooch crucible after drying it at 110°.

The results of the solubility experiments are given in the fol-

[1] Inaug. Dissert., Breslau, 1902; *Zischr. Elektrochem.*, **8**, 688 (1902).

lowing table, which for the sake of comparison also includes the results of Jander's measurements (indicated by the letter (J)). All concentrations are expressed in mols per liter. The solubility of mercuric sulphocyanate in water at 25° was found to be 0.0022 mol per liter.

TABLE I.—TEMPERATURE 25°.

Concentration of KSCN (a).	Solution taken for analysis cc.	Weight HgS.	Solubility of $Hg(SCN)_2$.	Increase of solubility of $Hg(SCN)_2$ (c).	Ratio total KSCN to combined $Hg(SCN)_2$ (a c).
0.101	..	.....	0.057	0.055	1.84 (J)
0.125	20	0.3276	0.071	0.069	1.81
0.248	..	.....	0.141	0.139	1.79 (J)
0.251	10	0.3272	0.141	0.139	1.80
0.542	..	.....	0.181	0.179	3.02 (J)
0.503	5	0.2715	0.233	0.231	2.18
0.730	..	.....	0.274	0.272	2.65 (J)
0.765	5	0.3449	0.298	0.296	2.58

At the lower concentrations the results agree very closely with those of Jander, and it is to be noted that the ratio $\frac{a}{c}$ though somewhat smaller than 2 approximates that value. This would indicate that there exists at these concentrations principally a complex with the ratio $\frac{n}{m} = 2$ mixed with a small amount of a complex for which that ratio is less than 2.

At the higher concentrations no agreement with Jander's results was obtained. This lack of agreement is to be explained, however, by the fact pointed out by Jander and illustrated by the following table, that the solubility decreases with the time of rotation.

TABLE II.—TEMPERATURE 25°.

Time of rotation.	Original concentration KSCN.	Solubility of $Hg(SCN)_2$.
4 hours	0.503	0.233
2 days	0.503	0.220
3 weeks	0.503	0.200

This phenomenon might be caused by the gradual separation of a solid complex salt and a consequent change in concentration of the potassium sulphocyanate. In this case a true equilibrium would be reached either on the complete disappearance of the mercuric sulphocyanate as solid phase, or when the potassium sulphocyanate had reached such a concentration as would correspond to

equilibrium with the two solid phases, the complex salt and the mercuric sulphocyanate. If the latter conditions are realized by keeping an excess of mercuric sulphocyanate present, the concentration of the final solution must be independent of the initial concentration of the potassium sulphocyanate solution used.

To test this point the following solubility experiments were carried out at 0°, a temperature more favorable to the formation of the complex. Two solutions of potassium sulphocyanate of different concentrations were shaken with a large excess of mercuric sulphocyanate for twenty hours, and then 20 cc. were analyzed for both mercury and potassium. The potassium was determined as sulphate by evaporating the filtrate from the hydrogen sulphide precipitate with sulphuric acid and strongly igniting. The results of the experiments are given in Table III.

TABLE III.—TEMP. 0°.

Initial KSCN conc.	Weight. K_2SO_4.	Weight. HgS	Final KSCN conc. a.	Solubility of $Hg(SCN)_2$.	Increase of solubility c.	$\frac{(a)}{c}$
0.125	0.1344	0.1909	0.0770	0.041	0.039	1.97
0.250	0.1332	0.1854	0.0765	0.040	0.038	2.01

The table shows very clearly the constancy of the final concentrations and therefore the correctness of the explanation given above. It is also to be noted that when a is put equal to the final potassium sulphocyanate concentration, the ratio $\frac{a}{c}$ becomes very nearly equal to 2.

From all these solubility experiments, we may draw the conclusion that at the concentrations in question a complex is formed in solution with the ratio $\frac{n}{m}=2$, the simplest assumption being a complex of the formula $K_2Hg(SCN)_4$. A solid complex salt also separates from solution but our experiments do not determine its composition.

III. FREEZING-POINT DETERMINATIONS.

The change of the freezing-point of a potassium sulphocyanate solution caused by successive additions of solid mercuric sulphocyanate offers another means of studying the constitution of the complex anion formed. Thus, in case no complex formation takes place on the addition of the mercuric sulphocyanate, the freezing-point would be lowered by an amount corresponding to the number

of mols added. Should one mol $Hg(SCN)_2$ combine with one SCN^- ion, the total number of mols in the solution, and hence the freezing-point would remain unchanged. Finally, if one mol of $Hg(SCN)_2$ were to unite with two or more SCN^- ions, the total number of mols in the solution would be decreased and the freezing-point correspondingly raised.

The results of such freezing-point determinations, which were made with a Beckmann apparatus in the usual way and with the usual precautions, are given in the following table:

TABLE IV.—FREEZING-POINT.

Conc. KSCN.	Conc. $Hg(SCN)_2$. C.	Raising of freezing-point Δ.	Δ/1.852.	$\frac{\Delta/1.852}{C}$
0.739	0.000	....	....	...
0.739	0.083	0.220	0.119	1.43
0.739	0.166	0.481	0.259	1.56
0.739	0.249	0.730	0.394	1.58
0.493	0.000	....	....	...
0.493	0.056	0.142	0.077	1.37
0.493	0.111	0.293	0.158	1.42
0.493	0.166	0.452	0.244	1.47
0.247	0.000	....	....	...
0.247	0.042	0.097	0.052	1.24
0.247	0.084	0.199	0.107	1.27
(0.247	0.126[1]	0.331	0.178	1.41)
0.124	0.000	....	....	...
0.124	0.042	0.072	0.039	0.93
0.124	0.063	0.124	0.067	1.06

In the fourth column of the table is given the quotient of the observed change of freezing-point Δ by the molecular change 1.852°. This should represent the total number of mols removed on the addition of the mercuric sulphocyanate. The last column contains the ratio of mols removed to mols of mercuric sulphocyanate added. An inspection of the last column of the table shows that at the concentrations 0.739 and 0.493 normal of the potassium sulphocyanate, for every mol of mercuric sulphocyanate added, a raising of the freezing-point is obtained which corresponds to the removal from the solution of one and a half mols, while at the lowest concentration 0.124 normal, for every mol $Hg(SCN)_2$ added, the change of freezing-point corresponds to a removal of only one mol from the solution. At the intermediate concentration 0.247 normal, the ratio of total number of mols removed

[1] Precipitation occurred.

from the solution to mols mercuric sulphocyanate added lies about midway between these limits. These changes might be explained by assuming that at the higher concentrations the complex anion $(Hg(SCN)_2)_2(SCN^-)_4$, at the lowest concentration $(Hg(SCN)_2)(SCN^-)_2$, and at the middle concentration a mixture of these two exist. Since the ratio $\frac{n}{m}$ for both of these complexes equal 2, these results agree with the conclusions drawn from the solubility experiments. The results described below, however, obtained from the measurement of the electromotive force of certain concentration cells at 0°, a method which is more reliable in concentrated solutions than the freezing-point one, show conclusively that only the simpler complex $(Hg(SCN)_2)(SCN^-)_2$ exists to an appreciable extent at any of these concentrations. It is probable therefore that at the higher concentrations the freezing-point change is not proportional to the change in molal concentration which would render the conclusions just referred to doubtful. In the dilute solution, where the theoretical significance of the freezing-point results is not doubtful, the results are in full accord with those obtained by the other methods.

IV. SOLUBILITY OF MERCUROUS SULPHOCYANATE IN POTASSIUM SULPHOCYANATE SOLUTION.

It is a well established fact that all mercurous salts decompose of themselves in aqueous solution into metallic mercury and the corresponding mercuric salt. This reaction mentioned by Behrend[1] for mercurous iodide, has beeen studied by Ogg[2] and Abel[3] and corresponds to the equilibrium:

$$(Hg_2)^{++} \rightleftarrows Hg^{++} + Hg.$$

As has been shown by Richards and Archibald[4] for the chloride, and by Abegg and Immerwahr[5] for the other halides, this decomposition goes much further in the presence of the alkali-metal halides or sulphocyanate. According to these investigations the explanation of this phenomenon is to be found in the fact that a

[1] *Ztschr. phys. Chem.*, **11**, 474 (1893).
[2] *Ibid.*, **27**, 285 (1898).
[3] *Ztschr. anorg. Chem.*, **26**, 377 (1901).
[4] *Proc. Am. Acad.*, **37**, 347 (1902); *Ztschr. phys. Chem.*, **40**, 385 (1902).
[5] *Ztschr. Elektrochem.*, **8**, 688 (1902).

part of the mercuric ions formed by the reaction disappear from the solution by chemical combination. Thus, in the action of potassium sulphocyanate on mercurous sulphocyanate, the mercuric sulphocyanate formed by the decomposition combines with the potassium sulphocyanate to form a complex, whereby the concentration of the free mercuric sulphocyanate and therefore of the mercuric ions is diminished. It will be seen from equation (4) below that, since the influence of the metallic mercury which is present as a solid phase is constant, a diminution of the concentration of the mercuric salt must cause a conversion of some of the mercurous salt into new mercuric salt and mercury, and then more mercurous salt must dissolve till equilibrium is again reached. As has been shown by Abegg and Immerwahr[1] for the bromide and iodide, the same equilibrium may be reached by shaking a solution of mercuric sulphocyanate in potassium sulphocyanate with metallic mercury.

The equilibria which occur in the subsequent discussion and the equations representing them are as follows:

Reactions in equilibrium. Equilibrium equations.

$$Hg_2(SCN)_2 \rightleftarrows Hg(SCN)_2 + Hg \qquad K = \frac{[Hg(SCN)_2]}{[Hg_2(SCN)_2]} \qquad (4)$$

$$m Hg(SCN)_2 + n SCN^- \rightleftarrows (Hg(SCN)_2)_m(SCN^-)_n$$

$$K_2 = \frac{[Hg(SCN_2)_m(SCN^-)_n]}{[Hg(SCN)_2]^m[SCN^-]^n}. \qquad (5)$$

$$Hg(SCN)_2 \rightleftarrows Hg^{++} + 2SCN^- \qquad K_3 = \frac{[Hg^{++}][SCN^-]^2}{[Hg(SCN)_2]}. \qquad (6)$$

$$Hg_2SCN_2 \rightleftarrows Hg_2^{++} + 2SCN^- \qquad K_4 = \frac{[Hg_2^{++}][SCN^-]^2}{[Hg_2(SCN)_2]}. \qquad (7)$$

To determine the formula of the complex which is formed, several methods may be employed. If we have, for example, mercurous salt present as solid phase, its concentration in the solution, and hence according to equation (4), that of the free mercuric salt, must be constant. If we now vary the concentration of the SCN^- ion by varying the concentration of the potassium sulphocyanate solution, the following equation must hold true,

$$\frac{[(Hg(SCN)_2)_m(SCN^-)_n]}{[SCN^-]^n} = K_2[Hg(SCN)_2]^m = K_5. \qquad (8)$$

[1] *Ztschr. Elektrochem.*, **8**, 688 (1902).

By assuming that the total mercuric sulphocyanate in solution is present in the form of the complex, which assumption is justified by the fact that mercuric sulphocyanate is but slightly soluble in water, we may calculate K_5 from the solubility of the mercurous sulphocyanate. If, as before, a represent the original concentration of the potassium suplhocyanate, and c that of the mercuric salt combined as complex, which here is substantially equal to the total concentration of the mercury, it follows in the solution saturated with mercurous sulphocyanate from equations (5) and (8) that

$$K_5 = \frac{\frac{c}{m}}{\left(a - \frac{n}{m}c\right)^n}. \qquad (9)$$

By choosing in equation (9) such values of m and n as cause the expression to remain constant, the formula of the complex may be determined.

With this purpose in view the solubility of mercurous sulphocyanate in solutions of potassium sulphocyanate of two different concentrations was measured. Equilibrium was obtained by rotating solutions of potassium sulphocyanate almost saturated with mercuric sulphocyanate with metallic mercury in a thermostat at 25° for several days. The dissolved mercury was determined as before by weighing as HgS.

TABLE V.—TEMPERATURE 25°.

Conc. KSCN. a.	Solution taken for analysis. cc.	Weight HgS.	Solubility of $Hg_2(SCN)_2$ as $Hg(SCN)_2$. c.	$K_5 = \frac{\frac{c}{m}}{\left(a - \frac{n}{m}c\right)^n}$			
				$m = 1.$ $n = 1.$	$m = 1.$ $n = 2.$	$m = 1.$ $n = 3.$	$m = 2.$ $n = 4.$
0.50	10	0.3248	0.140	0.39	2.89	272	29.9
0.25	10	0.1272	0.055	0.28	2.81	90	71.5

It is evident from the above table that the best constancy is obtained when m is made equal to 1, and n equal to 2, and that the formula of the complex is therefore $(Hg(SCN)_4)^{--}$.

V. ELECTROMOTIVE FORCE MEASUREMENTS.

The measurement of the electromotive force of concentration cells of the type

$$\mathbf{Hg} \,/\, \underset{\text{Conc. 1.}}{\left(Hg(SCN)_2 + KSCN\right)} \,//\, \underset{\text{Conc. 2.}}{\left(KSCN + Hg(SCN)_2\right)} \,/\, \mathbf{Hg},$$

furnishes another method of determining the formula of the complex, which has the advantage over that based on the solubility of the mercurous salt of being independent of the constancy of concentration of the mercurous and mercuric sulphocyanates. This method is, however, limited to such concentrations of mercuric sulphocyanate as correspond *in maximo* to the solubility of the mercurous sulphocyanate, since with higher concentrations the excess would precipitate when brought in contact with the mercury electrode.

From the electromotive forces, values of both m and n may be calculated according to the method of Bodländer,[1] as indicated below. For each solution of mercuric sulphocyanate in potassium sulphocyanate, the equation

$$\frac{[(Hg(SCN)_2)_m(SCN^-)_n]}{[Hg^{++}]^m[SCN^-]^{2m+n}} = \frac{K_2}{K_3{}^m} = K_1 \qquad (10)$$

or

$$[Hg^{++}]^m = \frac{1}{K_1}\frac{[(Hg(SCN)_2)_m(SCN^-)_n]}{[SCN^-]^{2m+n}}$$

must hold, where K_1 is the stability constant of the complex. From this it follows for two different solutions 1 and 2 that

$$\frac{[Hg^{++}]_1}{[Hg^{++}]_2} = \left(\frac{[(Hg(SCN)_2)_m(SCN^-)_n]_1[SCN^-]_2^{2m+n}}{[(Hg(SCN)_2)_m(SCN^-)_n]_2[SCN^-]_1^{2m+n}}\right)^{\frac{1}{m}}. \qquad (11)$$

Substituting for the concentrations in this equation their values in terms of a and c (see Sec. II), it becomes

$$\frac{[Hg^{++}]_1}{[Hg^{++}]_2} = \left(\frac{c_1\left(a_2 - \frac{n}{m}c_2\right)^{2m+n}}{c_2\left(a_1 - \frac{n}{m}c_1\right)^{2m+n}}\right)^{\frac{1}{m}}. \qquad (12)$$

When the concentrations of the SCN^- ion in the two solutions are equal, the equation simplifies itself to

$$\frac{[Hg^{++}]_1}{[Hg^{++}]_2} = \left(\frac{c_1}{c_2}\right)^{\frac{1}{m}}. \qquad (13)$$

This condition is fulfilled when $a_1 = a_2$ and when c_1 and c_2 are made small in comparison with it; that is, when the two solutions of potassium sulphocyanate are of the same strength, and in each of them is dissolved only a small proportion of mercuric sulphocyanate differing in the two cases.

[1] "Festschrift zum siebzigsten Geburtstage von Dedekind Braunschweig" (1901); see also *Ztschr. phys. Chem.*, **93**, 547 (1902).

Since now, according to the Nernst formula for concentration cells,

$$E_{25^\circ} = 0.0295 \log_{10} \frac{[Hg^{++}]_1}{[Hg^{++}]_2},$$

it follows from equation (13) that

$$E_{25^\circ} = \frac{0.0295}{m} \log_{10} \frac{c_1}{c_2} \text{ or } m = \frac{0.0295}{E_{25^\circ}} \log_{10} \frac{c_1}{c_2} \qquad (14)$$

where m naturally must be a whole number.

Having once established the value of m, the value for n may be calculated from equation (12) by measuring the electromotive force of any other cell, where the concentration of the SCN^- ions is different in the two solutions. This complicated equation is most easily solved by trial, which is rendered simple by the fact that n also must be a whole number.

By assuming the values of m and n obtained in this way, conversely, the ratio $\frac{[Hg^{++}]_1}{[Hg^{++}]_2}$ can be calculated from equation (12), and from this ratio the electromotive force of any given concentration cell determined. By comparison of the values thus calculated with the measured ones, we may decide how well this formula holds at all concentrations.

In order to obtain an absolute value for K_1 from equation (10) it is necessary to know the concentration of the mercuric ions in some one solution. Now the concentration of the mercurous ions in the normal calomel electrode has been calculated[1] to be

$$[Hg_2^{++}] = 6.3.10^{-18}.$$

In the investigation cited, this value was used as a basis for further calculations. Ley and Heimbucher[2] have, however, from the electromotive force of the concentration cell

$$Hg/Hg_2Cl_2,\ 1.0\ KCl \Big/\!\!\Big/ \frac{0.1\ Hg_2(ClO_4)_2}{2} /Hg,$$

correcting for the hydrolysis and dissociation of the mercurous perchlorate, obtained the more accurate value

$$[Hg^{++}_2] = 3.5.10^{-18}.$$

According to measurements of Abel,[3] the ratio of mercurous to

[1] Sherrill: *Ztschr. phys. Chem.*, **43**, 711 (1903).
[2] *Ztschr. Elektrochem.*, **10**, 303 (1504).
[3] *Ztschr. anorg. Chem.*, **26**, 377 (1901).

mercuric ions $\frac{[Hg_2^{++}]}{[Hg^{++}]}$ when in equilibrium with metallic mercury is equal to 120. Using the value given above by Ley and Heimbucher, it follows from this that the concentration of the mercuric ions in the normal electrode is

$$[Hg^{++}] = \frac{3.5 \times 10^{-18}}{120} = 2.9 \times 10^{-20}.$$

We therefore measured the electromotive force of the various sulphocyanate solutions in combination with a normal electrode. From a knowledge of these values for the normal electrode, the concentration of the mercuric ions in the solution may be calculated from the Nernst equation for concentration cells. By substituting the values thus found in equation (10), we obtain the stability constant K_1 for the complex anion in question.

The measurements of the electromotive force were made according to the Poggendorf compensation method, using a capillary electrometer. The following table contains the results and calculations with different concentrations of potassium sulphocyanate containing varying amounts of mercuric sulphocyanate.

TABLE VI.—TEMPERATURE 25°.

Number.	Conc. KSCN. a.	Conc. $Hg(SCN)_2$. c.	E. M. F. against N E.	E. M. F. against solution No. 8.		Conc. Hg^{++}.	$K_1 = \frac{[Hg(SCN)_4^{--}]}{[Hg^{++}][SCN^-]^4}$.
				Meas.	Calc.		
1	1.53	0.400	0.078	0.091	0.099	6.6×10^{-23}	21.4×10^{21}
2	1.53	0.200	0.106	0.064	0.068	7.7×10^{-24}	15.7×10^{21}
3	1.53	0.100	0.120	0.049	0.051	2.4×10^{-24}	13.1×10^{21}
4	1.53	0.050	0.132	0.037	0.039	9.9×10^{-25}	11.9×10^{21}
5	1.53	0.025	0.141	0.028	0.028	4.8×10^{-25}	10.8×10^{21}
6	1.53	0.0125	0.149	0.020	0.018	2.6×10^{-25}	9.5×10^{21}
7	1.53	0.00625	0.160	0.009	0.009	1.1×10^{-25}	10.8×10^{21}
8	1.53	0.00313	0.169	0.000	....	5.5×10^{-26}	10.4×10^{21}
9	1.02	0.200	0.056	0.113	0.116	3.6×10^{-22}	3.8×10^{21}
10	1.02	0.133	0.084	0.085	0.081	4.1×10^{-23}	10.2×10^{21}
11	1.02	0.0665	0.100	0.069	0.067	1.2×10^{-23}	9.0×10^{21}
12	1.02	0.0333	0.112	0.057	0.055	4.6×10^{-24}	9.0×10^{21}
13	1.02	0.0166	0.122	0.047	0.044	2.1×10^{-24}	8.0×10^{21}
14	1.02	0.00831	0.132	0.037	0.035	9.9×10^{-25}	8.0×10^{21}
15	1.02	0.00416	0.140	0.029	0.027	5.1×10^{-25}	7.7×10^{21}

Number.	Conc. KSCN. a.	Conc. $Hg(SCN)_2$. c.	E. M. F. against N. E.	E. M. F. against solution No. 8.		Conc. Hg^{++}.	$K^1 = \frac{[Hg(SCN)_4^{--}]}{[Hg^{++}][SCN^-]^4}$
				Meas.	Calc.		
16	0.765	0.200	0.043	0.126	0.127	1.0×10^{-21}	10.6×10^{21}
17	0.765	0.100	0.071	0.098	0.096	1.5×10^{-22}	7.0×10^{21}
18	0.765	0.050	0.088	0.081	0.079	3.1×10^{-23}	8.8×10^{21}
19	0.765	0.025	0.100	0.069	0.066	1.2×10^{-23}	8.2×10^{21}
20	0.765	0.0125	0.111	0.058	0.056	5.1×10^{-24}	8.2×10^{21}
21	0.765	0.00625	0.121	0.048	0.046	2.3×10^{-24}	8.2×10^{21}
22	0.765	0.00313	0.130	0.039	0.037	1.2×10^{-24}	8.6×10^{21}
23	0.503	0.140	0.025	0.144	0.147	4.1×10^{-21}	13.7×10^{21}
24	0.503	0.070	0.057	0.112	0.113	3.4×10^{-22}	11.3×10^{21}
25	0.503	0.035	0.073	0.096	0.095	9.3×10^{-23}	10.4×10^{21}
26	0.503	0.0175	0.086	0.083	0.082	3.6×10^{-23}	10.2×10^{21}
27	0.503	0.00875	0.097	0.072	0.072	1.5×10^{-23}	10.2×10^{21}
28	0.503	0.00438	0.106	0.063	0.062	7.1×10^{-24}	1.0×10^{21}
29	0.503	0.00219	0.116	0.053	0.052	3.4×10^{-24}	10.2×10^{21}
30	0.251	0.035	0.027	0.142	0.142	3.6×10^{-21}	9.3×10^{21}
31	0.251	0.0175	0.043	0.126	0.128	1.0×10^{-21}	8.2×10^{21}
32	0.251	0.00875	0.057	0.112	0.110	3.4×10^{-22}	8.6×10^{21}
33	0.251	0.00438	0.067	0.102	0.099	1.5×10^{-22}	8.4×10^{21}
34	0.251	0.00219	0.077	0.092	0.089	7.1×10^{-24}	8.0×10^{21}
						Mean,	9.7×10^{21}

The value for m was calculated from the concentration cell consisting of solutions 7 and 8 by substituting the values in equation (14) as follows:

$$m = \frac{0.0295}{0.009} \log. \frac{0.00625}{0.00313} = 0.99.$$

Values approximately 1 are also obtained by calculating m from the concentration cells consisting of solutions 14 and 15, 21 and 22, 28 and 29, 32 and 34.

The value for n may now be obtained from any concentration cell where the concentration of the SCN^- ions in the two solutions is different, for example from the cell consisting of solutions 1 and 7. It is found to be approximately equal to 2, and the formula of the complex ion is therefore $Hg(SCN)_4^{--}$. The constancy of the K_1 values, and the good agreement of the measured electromotive

forces with those calculated under this assumption as to the complex ion show conclusively the existence of this complex throughout this whole range of concentration.

This conclusion is in agreement with that drawn from all the other methods employed except the freezing-point determinations at the higher potassium sulphocyanate concentrations (see Sec. III), where there were indications, though probably unreliable ones, that m was equal to 2 and n equal to 4. To see whether the complex really had polymerized at 0°, electromotive force measurements were made at that temperature with the following results:

TABLE VII.—TEMP. 0° C.

Sol. No.	Conc. KSCN.	Conc. $Hg(SCN)_2$.	E. M. F. against normal electrode.	E. M. F. against Sol. No. 1.	
				Measured.	Calculated.
1	1.02	0.200	0.094	0.000	0.000
2	1.02	0.100	0.115	0.021	0.023
3	1.02	0.050	0.128	0.034	0.038
4	1.02	0.025	0.139	0.045	0.051
5	1.02	0.0125	0.148	0.054	0.061
6	1.02	0.00625	0.157	0.063	0.069
7	1.02	0.00313	0.166	0.072	0.077

Here, as before, the calculated values of the electromotive force are found to agree well with the measured ones when it is assumed that $m = 1$ and $n = 2$, and we may draw the conclusion that here as well as at 25° the complex $Hg(SCN)_4^{--}$ is the only one which exists to an appreciable extent in the solution.

When mercurous sulphocyanate is present as a solid phase in a potassium mercuric sulphocyanate solution, it is possible by using the concentration of the mercurous ions in the normal electrode (see above) to calculate its solubility product; for the SCN^- ion concentration is known, and the Hg_2^- ion concentration may be calculated from the electromotive force measurement.

Furthermore, the solubility of mercuric sulphocyanate in any particular strength of potassium sulphocyanate may be calculated from electromotive force measurements and from the stability constant K_1, by solving for c in the equation

$$K_1 = \frac{\frac{c}{m}}{[Hg^{++}]\left(a - \frac{n}{m}c\right)^{2m+n}},$$

and this calculated value of the solubility compared with that analytically determined. Table VIII contains the results of such measurements and calculations with two solutions of potassium sulphocyanate saturated with mercuric sulphocyanate.

TABLE VIII.—TEMP. 25°.

Concentration. KSCN. a.	E. M. F. against normal electrode.	Conc. Hg^{++}.	Conc. Hg_2^{++}.	Solubility of $Hg(SCN)_2$. Analytically determined.	Solubility of $Hg(SCN)_2$. Calculated.	Sol. product. $[Hg_2^{++}]\times[SCN^-]^2$
0.50	0.028	3.3×10^{-21}	4.0×10^{-19}	0.14	0.13	1.9×10^{-20}
0.25	0.018	7.1×10^{-21}	8.5×10^{-19}	0.055	0.045	1.7×10^{-20}

The agreement between the fifth and sixth columns is further evidence of the existence of the complex $Hg(SCN)_4^{--}$.

From the solubility product (s. p.) of $Hg_2(SCN)_2$ may be calculated the concentration of the mercurous ions in a saturated solution of this salt in pure water, which is identical with its solubility if complete dissociation be assumed, for in pure water

$[SCN^-] = 2[Hg_2^{++}]$ and therefore s. p. $= 4[Hg_2^{++}]^3$ or

$$[Hg_2^{++}] = \sqrt{\frac{\text{s. p.}}{4}} = \sqrt[3]{\frac{1.8 \times 10^{-20}}{4}} = 1.7 \times 10^{-7}$$

VI. COMPARISON OF THE RESULTS WITH THOSE OBTAINED WITH THE MERCURIC HALIDE COMPLEXES.

A comparison of the stability constants of the various mercuric complexes thus far investigated shows the relative tendency of the halogens and of the cyanogen and sulphocyanogen groups to form complexes. These constants are brought together in the following table.

TABLE IX.

Complex salt.	Stability constant.[1]
K_2HgCl_4	1.6×10^{16}
K_2HgBr_4	7.7×10^{21}
$K_2Hg(SCN)_4$	9.7×10^{21}
K_2HgI_4	3.5×10^{30}
$K_2Hg(CN)_4$	4.6×10^{41}

[1] The stability constants for the chloride, bromide, iodide and cyanide complexes were recalculated from the values given by Sherrill (*Loc. cit.*), using the concentration of mercurous ions in the normal electrode obtained by Ley and Heimbucher (*Loc. cit.*).

According to the above table, the tendency towards complex formation increases in the following order: Cl, Br, SCN, I, CN. Grossman,[1] from a large collection of qualitative data, and Bodländer and Eberlein,[2] by comparing the stability constants of the corresponding complex silver salts, have arrived at the same conclusion.

According to Abegg and Bodländer[3] with different salts of the same metal, the solubility as a rule increases with increasing electroaffinity of the anion. The order of decreasing solubility should therefore be the same as that of increasing stability of the complex.

The following table shows the solubility in water of the mercurous salts, the salts being arranged in the order of decreasing solubility.

TABLE IX.

Cl.[4]	SCN.	Br.[5]	I.[5]
0.8×10^{-6}	1.6×10^{-7}	5.6×10^{-8}	2.5×10^{-10}

Here, as Bodländer and Eberlein[6] also found by comparing the solubility products of the silver halides, Br and SCN have reverse positions from what they do in the series of the stability constants of the complex, but, as the differences in the two values are not large in either case, this is not a serious anomaly.

VII. SUMMARY.

The existence in aqueous solution of a complex salt of the composition $K_2Hg(SCN)_4$ has been shown by a number of physicochemical methods. Its degree of stability has been determined, and incidentally the solubility-product of mercurous sulphocyanate has been deduced.

1. The increase of solubility of mercuric sulphocyanate caused by the addition of potassium sulphocyanate was found, when expressed in mols per liter, to be always approximately equal to one-half of the number of mols of potassium sulphocyanate added. This indicated in saturated solutions the quantitative formation of a complex of the general formula

$$K_{2m}Hg_m(SCN)_{4m}.$$

2. The change of the freezing-point of moderately dilute solu-

[1] *Ztschr. anorg. Chem.*, **37**, 433 (1903).
[2] *Ibid.*, **39**, 238 (1904).
[3] *Ibid.*, **20**, 458 (1899).
[4] Ley and Heimbucher (*Loc. cit.*).
[5] Recalculated from values of Sherrill (*Loc. cit.*).
[6] *Loc. cit.*

tions of potassium sulphocyanate caused by the addition of varying amounts of mercuric sulphocyanate was found to correspond to a removal from the solution of one mol for every mol of mercuric sulphocyanate added. This, taken in conjunction with the preceding conclusion, can be explained only by the formation of the complex $K_2Hg(SCN)_4$.

3. The solubility of mercurous sulphocyanate in potassium sulphocyanate was determined. This solubility results in virtue of the following reactions:

$$Hg_2(SCN)_2 \rightleftarrows Hg(SCN)_2 + Hg,$$

$$m\ Hg(SCN)_2 + n\ SCN^- \rightleftarrows (Hg(SCN)_2)_m(SCN^-)_n.$$

The law of mass acton therefore requires that, when mercurous sulphocyanate as solid phase is in equilibrium with a solution of potassium sulphocyanate, the following equation must hold.

$$\frac{[(Hg(SCN)_2)_m(SCN^-)_n]}{[SCN^-]^n} = K_1[Hg(SCN)_2]^m = K$$

Since mercuric sulphocyanate is but slightly soluble in water, the total amount of mercuric salt in solution may be taken as a measure of the concentration of the complex. It is therefore possible by assuming the existence of any one complex, to calculate K from the solubility of the mercurous salt and the concentration of the potassium sulphocyanate. From the solubility of mercurous sulphocyanate in different concentrations of potassium sulphocyanate, the best constancy of the K values was obtained by assuming the complex to be $K_2Hg(SCN)_4$.

4. By measuring the electromotive force of concentration cells of the type

$$Hg/\underset{\text{Conc. 1.}}{(Hg(SCN)_2 + KSCN)}\ /\ \underset{\text{Conc. 2.}}{(KSCN + Hg(SCN)_2)}/Hg,$$

and applying the law of mass action to the results, the formula of the complex salt was also found to be $K_2Hg(SCN)_4$.

5. From the electromotive force of such solutions measured against the normal calomel electrode, in which the concentration of the mercury ions is known, the concentration of the mercuric ions in the solution in question could be calculated, and from this was derived the stability-constant of the complex, which is defined by the equation

$$K = \frac{[Hg(SCN)_4^{--}]}{[Hg^{++}][SCN^-]^4}$$

The constancy of this expression gave evidence of the existence of the above complex salt throughout the whole range of concentration taken.

6. A comparison of the value of this stability-constant (9.7×10^{21}) with those of the corresponding mercuric halide complexes showed that the relative tendency of the halogens and of the cyanogen and sulphocyanogen groups to form complexes increases in the following order: Cl, Br, SCN, I, CN.

7. In solutions where the mercury electrode caused precipitation of mercurous sulphocyanate, the concentration of the mercurous ions was calculated from the electromotive force measured against the normal electrode. The concentration of SCN— ions in such solutions was calculable from the concentration of the potassium sulphocyanate and the solubility of the mercurous salt. From these two values the solubility product of mercurous sulphocyanate, $[Hg_2^{++}][SCN^-]^2$, was calculated to be 1.8×10^{-20}.

In conclusion we wish to express to Prof. A. A. Noyes our sincere thanks for his friendly interest in the investigation, and for the material assistance he has given us.

MOLECULAR WEIGHT DETERMINATIONS BY MEANS OF PLATINUM THERMOMETERS.

By H. T. Barnes, E. H. Archibald, and D. McIntosh.

Received October 18, 1904.

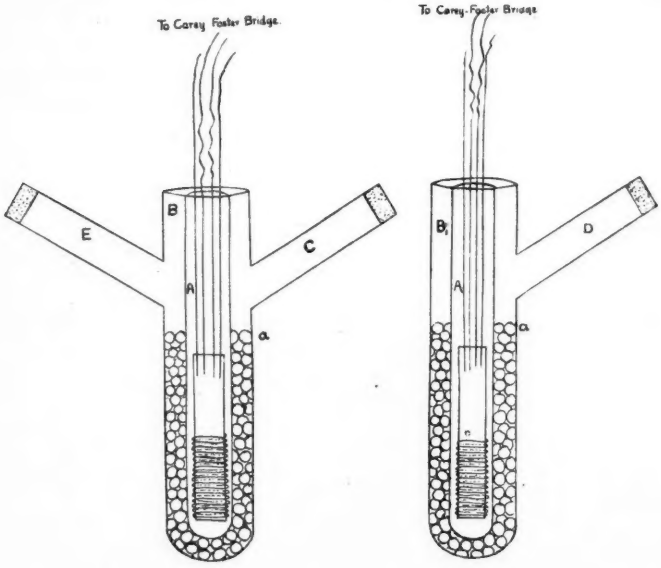
In the course of an extended investigation on the properties of liquefied gases, we found it necessary to determine the molecular weights of some substances dissolved in these liquids for the purpose of comparison with conductivity measurements; and since these measurements were to be made at temperatures as low as —80 C., we were compelled to modify the apparatus ordinarily used.

We have, therefore, used platinum thermometers; and as these have only, so far as we are aware, been employed in determinations of the rise in boiling-point by Noyes[1] and Abbott and that by a different method, we give here a description of our apparatus and some results of determinations of the molecular weights of inorganic salts when dissolved in water.

[1] *Ztschr. phys. Chem.*, **23**, 63 (1897).

Our bridge was of the Carey-Foster type and of such a resistance that 1.670 cm. on the bridge wire represented a difference in temperature of 1° C. in our platinum thermometers; with the galvanometer used the bridge could be read with certainty to 0.5 mm., *i. e.*, to 1/30° C.

The method,[1] as will be seen from the diagram, was a differential one. Two thermometers, exactly equal in resistance, each consisting of about 1 meter of 6-mil wire wound on a mica frame are, with their compensating leads, placed in the two tubes A and A_1, which are closed at the lower end and sealed into the larger



tubes B and B_1. B and B_1 contain glass beads to prevent bumping and are filled with the solvent to the mark *a*, the amount in A being carefully weighed. The tubes are connected through C and D to condensers, E is tightly stoppered and the apparatus is heated in an air- or oil-bath. When the liquid is boiling freely the zero point of the bridge is found, and a weighed portion of the substance whose molecular weight is to be determined is introduced into A

[1] For temperature measurements with platinum thermometers, see Barnes: *Trans. Roy. Soc.*, Series A., 199 (1902).

through the side-arm E. The point at which the galvanometer shows no deflection is then ascertained, and from the data the molecular weight is calculated in the usual manner.

The following determinations with the chloride, nitrate, and sulphate of potassium were made with water as solvent.

DETERMINATIONS (K = 510).

Salt.	Rise of B. P.	Molecular weight.	
	Potassium chloride.		
0.835	0.42	37.0	H_2O = 27.4 grams.
1.622	0.81	37.3	
2.295	1.19	35.9	
2.900	1.54	35.1	
	Potassium nitrate.		
1.691	0.54	58.3	H_2O = 27.4 grams.
2.207	0.67	61.3	
2.685	0.85	58.8	
	Potassium sulphate.		
0.887	0.28	82.4	
1.570	0.53	77.1	H_2O = 19.6 grams.
2.344	0.86	70.9	
2.960	1.08	71.3	
3.693	1.29	74.5	

The apparatus is convenient and in some ways much superior to that in which mercury thermometers are used, since neither adjustment for liquids having different boiling-points nor tapping device is necessary; changes in atmospheric pressure can introduce no error and the thermometers can be made of any degree of sensitiveness required.

MCGILL UNIVERSITY, MONTREAL,
October, 1904.

THE SOLUBILITY OF GYPSUM AS AFFECTED BY SIZE OF PARTICLES AND BY DIFFERENT CRYSTALLOGRAPHIC SURFACES.

BY G. A. HULETT.

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IT HAS been shown[1] that the effect of the size of particles on the solubility of the solid is detectable and measurable; the smaller particles not only dissolve more rapidly, but have a greater solubility. The theoretical possibility of such a relation was pointed

[1] Ostwald: *Ztschr. phys. Chem.*, **34**, 495 (1900); Hulett: *Ztschr. phys. Chem.*, **37**, 385 (1901).

out by P. Curie,[1] while Ostwald[2] has made use of the idea to explain the well-known fact that a precipitate in contact with its solution, will, in time, become coarse-grained. The explanation of the phenomenon is based on the following considerations: The boundary between a solid and a liquid is the seat of a certain amount of energy due to the surface energy of the liquid; if this surface is increased by powdering the solid, the total surface energy is correspondingly increased. Further, it is a generally observed fact that the form of a substance which has the greater free energy is the more soluble, has the greater vapor pressure, and is the least stable form,[3] *e. g.*, allotropic modifications of substances have different solubilities and the unstable form is always the more soluble. The phenomenon is hardly analogous to the well-known behavior of liquid drops of different sizes. Small drops in the vicinity of large ones grow smaller and disappear, while the large ones grow larger,[4] and the reason for this is quite clear. It is known that the curved surface of a liquid has a greater vapor pressure than a plain or less curved surface, therefore a distillation takes place. The similarity between the vapor pressure of liquids and the solution pressure of solids has suggested to some the analogy between the facts just mentioned and the behavior of solid particles of different sizes in contact with the solution. But we cannot assume that the surfaces of the particles of a powder are curved, or, if that is granted we do not know that a curved surface of a solid or a sharp edge, has a greater solution pressure than a plane surface of the same substance.

In order to get some idea of the energy on the surface between a solid and its solution, use was made of the previous work on gypsum.[5] A solution of gypsum saturated at 25° contains 2.080 grams $CaSO_4$ in a liter (0.01530 mol in a liter). If this solution is shaken with powdered gypsum, the concentration increases rapidly to a maximum, and then decreases and finally reaches the original concentration. The change can be easily and accurately followed by measuring the conductivity of the solution at intervals. In one experiment (*Loc. cit.*, p. 393) the concentration reached 2.542 grams $CaSO_4$ in a liter in a minute, and then began

[1] *Bull. Soc. Min.*, **8**, 145 (1885).
[2] *Anal. Chem.*, pp. 15 and 23.
[3] Van't Hoff: *Vorlesungen*, II, 124; *Allgem. Chem.*, II, **2**, 860.
[4] Ostwald: *Grundriss d. allgem. Chem.*, pp. 152 and 318.
[5] *Ztschr. phys. Chem.*, **37**, 388 (1901).

to decrease, and finally reached the original value of 2.080 grams $CaSO_4$ in a liter. The powder used was ground as fine as possible in an agate mortar and contained many exceedingly fine particles, mere points under the highest magnification, while the powder obtained after nine days careful agitation at 25° showed no particles less than 1 μ (0.001 mm.) in diameter, but there were many of this diameter. It is to be noted that the smallest particles having proportionately the greater surface, as well as being the more soluble, will play the greatest rôle in the process of dissolving, and in dissolving become even smaller and more soluble. The effect is accumulative. All those particles below a certain size will completely disappear, supersaturating the solution, and finally be deposited on the larger particles. In view of this it is difficult to estimate the size of particles which would be in equilibrium with the above-observed solution containing 2.540 grams of $CaSO_4$ in a liter, certainly less than 0.1 μ; but assuming that the particles which were in equilibrium with the solution were as large as 0.1 μ, we can calculate the surface energy on a cubic centimeter of the gypsum powder (about 2.5 grams). A cubic centimeter with 6 sq. cm. surface if reduced to particles 0.1 μ edge, would have a surface of 600,000 sq. cm. Increasing the surface of the gypsum solution by this amount would require about 4.8×10^7 ergs, since it requires about 80 absolute units to increase the surface of the solution 1 sq. cm. This is over a calorie in heat units and probably is under the true value that caused the 20 per cent. increase in the solubility. This is not much energy, but compares favorably with the difference in energy of allotropic modifications, and it is not unreasonable to assume that it is sufficient to account for the observed difference in solubility; however, in the absence of more exact proof, other possible causes have been considered, and especially the idea that different crystallographic planes may have different solubilities. If in powdering gypsum the more soluble planes predominate, an explanation of the observed facts is obvious.

In view of the different physical properties of different planes of a crystal it seems reasonable to assume that they also have different solubilities. There is an interesting article, by F. Rinne,[1] on "Richtungsverschiedenheiten bezuglich der Löslichkeit von Gypsspaltblättchen." The author prepared thin circular disks of gyp-

[1] *Centrbl. f. Min. Geol. and Paleont.*, 1904, p. 116.

sum parallel to $_{\infty}P\breve{\infty}(010)$, and exposed these to the action of dilute hydrochloric acid, which is a good solvent for gypsum. It was observed that the circular disks, on dissolving, became elliptical, the edges in some directions dissolved *more rapidly* than in others, the action was greatest along $P\bar{\breve{\infty}}(101)$, and least on $\bar{\infty}P\bar{\infty}(100)$.[1] Similar results are referred to under Coromila's Inaugural Dissertation, Tübingen, 1877. This work shows that the *rate* of solution is different in different directions. The existence of "Aetzfiguren" also proves[2] that there must be differences in the rate of solution for different planes of the same crystal; but have the different planes of a crystal different solubilities? The term solubility should be more clearly defined and entirely differentiated from any idea of rate. *Solubility is measured by the concentration of the solution which is in final equilibrium with the solid,* and is independent of the rate at which this equilibrium is established.

In order to test the solubility of different planes of gypsum it seemed only necessary to determine whether a solution which was in equilibrium with one plane was also in equilibrium with another, and the conductivity of gypsum solutions affords such an exact and simple method of determining the concentration[3] that the determination seemed feasible, but no positive results were obtained, and in view of the exceeding slowness with which the system gypsum-solution comes to equilibrium[4] more evidence was sought.

In all the previous work the concentration of the solution in equilibrium with thin cleavage plates was taken as the measure of the solubility of gypsum; with such plates the clinopinacoid $_{\infty}P\breve{\infty}(010)$ so largely predominates that we can regard the 2.080 grams in liter as the concentration which is in equilibrium with (010) at 25°. Some exceedingly clear and perfect crystals of gypsum were procured on which the faces (010) formed only about one-third of the total surface, the other faces present being $_{\infty}P(110)$ and $-P(111)$. These crystals were rinsed with the above-mentioned saturated solution, dried, weighed, and then the various diameters carefully measured with a micrometer caliper. The crystals with about an equal volume of the above solution, saturated in

[1] See original.
[2] Nernst's "Theoretical Chemistry," 4th ed., p. 88.
[3] *Ztschr. phys. Chem.*, **37**, 385 (1901), and **42**, 577 (1903); This Journal, **25**, 667 (1902).
[4] This Journal, **25**, 676 (1902).

respect to (010), were sealed off in a little Jena glass tube, placed in a thermostat (25°) and agitated from time to time. If the solution is not also in equilibrium with the faces (110) and (111), it will either dissolve from these faces or deposit on them, and will then no longer be in equilibrium with (010); in short, there will be a continual transference of material from the more soluble to the less soluble faces, and it will be merely a question of time until the effect on the different diameters becomes measurable. The tube with its contents remained at 25° ± 0.1 from April 7th to June 6th, with frequent gentle rotations. On opening the tube the solution had a conductivity $\lambda_{25} = 0.002210$, whereas the original solution was $\lambda_{25} = 0.002208$, and there was no detectable difference in the measurements of the various diameters of the crystals. There had, however, been a slight loss in weight of the three crystals of 1.4 mg. (their total weight being 9,2550 grams). The crystals were again sealed off in a tube with some gypsum solution ($\lambda_{25} = 0.002208$), and in a second similar tube some of the solution only. These tubes, frequently rotated, were maintained at 25° from June 6th to August 10th, when the solution from the crystals showed the conductivity $\lambda_{25} = 0.002209$, while the solution from the second tube without gypsum present showed $\lambda_{25} = 0.002191$. Evidently the Jena glass removed gypsum from solution, and the crystals had again lost about 1 mg. The various diameters were again very carefully measured and checked within the limit of error of measurement (±0.01 mm.) to the two previous measurements. The three crystals had been five months in contact with a solution which must have been in equilibrium with all the faces present and even a fracture on one of the crystals. The concentration of this solution was 2.080 grams in a liter and $\lambda_{25} = 0.002208$.

It can be concluded from the above that if there is a difference in solubility of the various planes it can not be detected by the above method, that it plays no rôle in the effect of size of particles on the solubility, and this constitutes a further proof that surface energy is the real cause.

The work so far has suggested some considerations in connection with solubility determinations that seem to deserve attention. If a solvent is to be saturated with a powdered substance, and the solubility is considerable, the finest particles and those that become

fine by dissolving, will play the largest rôle in the process, as pointed out above. If after all these particles have disappeared the solution is still undersaturated, then the system slowly approaches the concentration that is in equilibrium with a plain surface from the undersaturated side. If, however, the solubility is small, say 1 per cent. or less, there may be a sufficient number of particles of 2 μ or less present, or produced, to rapidly bring the concentration above the normally saturated solution, and the system then approaches the concentration that is in equilibrium with a plain surface from the *supersaturated side*, while it has been generally assumed in such cases that the point was being approached from the undersaturated side. This is surely the case with gypsum, as the following experiments prove.

Fifty grams of clear, chlorine-free gypsum was powdered, and brought together with 500 cc. of conductivity water, all at 25°. The system was shaken and in three minutes a sample removed.

Time from mixing. Minutes.	Conductivity.	Concentration Gram $CaSO_4$ in L.
3	0.002350	2.254
25	0.002320	2.216
70	0.002301	2.192

From here on the decrease was continually slower, requiring seventeen days and careful handling to bring the system to final equilibrium. The previous work has shown that the conductivity is an exceedingly accurate measure of the concentration. The relation between concentration and conductivity has been carefully determined.[1] A few suspended particles between the electrodes play no rôle, while the heat of solution which might have affected the first determination is very small and negative. The system was in a tube some 20 x 5½ cm., drawn down and sealed off. Above the thermostat was a motor-driven shaft, and from the shaft little belts extended down into the bath. The above tube rested in the loops of these little belts, with rubber rings to keep the belts in place. Thus the tube was rotated around its longer axis in the bath and at any desired rate. The powdered gypsum was thus spread out in a long layer and slowly rolled "down hill" as the tube revolved. Previous work[2] has shown that this system, gypsum-solution, is one of the most difficult to bring to final equilibrium. With too

[1] *Ztschr. phys. Chem.*, **42**, 581 (1903).
[2] *Ibid.*, **37**, 394.

rapid agitation the concentration may remain 5 per cent. too great, while on standing practically no change takes place. The above system required seventeen days of very slow rotation to come to final equilibrium. Two hundred cc. of the clear solution were finally removed, evaporated to dryness and the residue ignited, taking all precautions previously found necessary.[1] 0.4167 gram $CaSO_4$ was obtained (which, moistened with sulphuric acid and again ignited, gave the same weight). This is 2.083 grams $CaSO_4$ in a liter. Another experiment was tried where *only* 5 grams of finely powdered gypsum were shaken with 500 cc. of water (one-tenth the amount of powder used in the previous case).

Time for mixing. Minutes.	Conductivity.	Concentration. Grams $CaSO_4$ in L.
2	0.002290	2.167
8	0.002303	2.193
Hours.		
12	0.002241	2.112
198	0.002230	2.103

For lack of time this experiment was not carried further, but many experiments have shown that the concentration will finally decrease to 2.080 grams in a liter.

For inorganic substances gypsum is very exceptional in its behavior, requiring a half day or more to saturate the solution from the undersaturated side, where only plates of gypsum are used.[2] Under similar conditions most substances would saturate a solution in an hour or so. From the supersaturated side the system, gypsum-solution, exhibits an even more striking exception, requiring weeks and very careful handling to bring to final equilibrium, and in view of all the facts brought out it is not surprising that there have been great discrepancies in the solubility determinations of gypsum, as given by various investigators. Lately F. K. Cameron[3] has laid considerable stress on a value obtained by him of 2.120 grams $CaSO_4$ in a liter at 25° as the solubility of gypsum under ordinary conditions, while Droez,[4] working with equal care, obtained 2.180 grams $CaSO_4$ in a liter at 25°, etc. But it is to be concluded that the systems analyzed by these investigators were not in final equilibrium. With varying amounts of gypsum powder and solvent, different results will be obtained unless care is taken

[1] This Journal, **24**, 672 (1902).
[2] *Ibid.*, **24**, 676 (1902).
[3] *J. Phys. Chem.*, **7**, 571.
[4] *Ber. d. chem. Ges.*, 1877, p. 330.

to bring each system to final equilibrium, and the solution then obtained contains only 2.080 grams $CaSO_4$ in a liter, from whichever side approached. The above sources of error should be guarded against in solubility work where the solubility is small. In attempting to approach the equilibrium from both sides, as is commonly done, it may happen that the point is *approached only from the supersaturated side,* as pointed out above.

If the bottom of an Erlenmeyer flask is covered with large particles or crystals of the solid, and the solvent rotated over these crystals by a motor-driven Schultz stirrer, none of the above difficulties will be encountered; further, the solution is always perfectly clear and free of particles, which is often a very considerable advantage. A supersaturated solution may also be rotated over the same crystals, and the equilibrium approached from both sides. By this method the solubility of gypsum from 0° to 100° has been determined by Hulett and Allen,[1] and the results in this paper show that the values obtained at that time, where the cleavage plane very largely predominated, are also the values for any plane of gypsum.

UNIVERSITY OF MICHIGAN,
October, 1904.

[CONTRIBUTIONS FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE, No. 57.]

THE ESTIMATION OF POTASH IN SOILS, PLANTS AND FERTILIZERS.

BY F. P. VEITCH.

Received November 2, 1904.

CONSIDERABLE interest has been displayed in improving standard methods for the estimation of potash in soils, plant substances and fertilizers during the past three or four years.[2]

It is now generally recognized that in the case of fertilizers, potash added in the form of salts is seldom entirely accounted for in the analysis of the completed mixtures, and this latter fact has led to much complaint from the manufacturers. It has been found

[1] This Journal, **24**, 667 (1902).

[2] *Chem. News*, **79**, pp. 135-136; *J. Chem. Soc.* (London), **77**, 1076; *Stat. Spar. Agr. Ital.*, **33**, 454; *Ann. Chim. Anal. et. Appl.*, **5**, 289; *Ztschr. anal Chem.*, **39**, 481; **40**, 385; **40**, 569; *Chem. Ztg.*, **26**, 1014; **28**, 210; **28**, 36; *Ztschr. angew. Chem.*, **15**, 1263; *Ztschr. anorg. Chem.*, **36**, 323; **36**, 325; this Journal, **25**, 416; **25**, 491; **26**, 297.

that low results are obtained both when organic matter is present in the mixed fertilizer and also when the mixture consists only of acid phosphates and of potash salts.[1]

In the case of plant substances and of soils no particular complaint has been made as to the accuracy of the official methods, but the necessity of first removing iron, alumina, lime and phosphoric acid, and of washing thoroughly this precipitate in order to remove all potash from it, makes the estimation very tedious and slow. In addition to this, the use of, and the subsequent removal of, large quantities of reagents, certainly cannot add to the accuracy of the estimation. There has been good reason then, both from the standpoint of accuracy and of convenience, for the efforts to simplify and shorten the procedure in the estimation of potash in the above-mentioned materials.

In this effort it is unfortunate that more attention has not been given to the method proposed by Moore,[2] as in it many of the usual preliminary operations are omitted and the method is at once the simplest and the shortest and possesses apparently a high degree of accuracy. The method has been used on soils and plants in the Bureau of Chemistry by several independent workers with highly satisfactory results, and in presenting my own results with the original method, and with modifications of it, and in studying

[1] It is an open question how much of this potash which is insoluble in water should be regarded as available to plants, and it is to be doubted if it can be justly regarded as within the meaning of the law; most, if not all, state laws calling for "water-soluble potash."

[2] This Journal, **20**, 342. The method is as follows: The material under examination is brought into solution in acid, ammonium salts, and organic matter destroyed with aqua regia and the excess of acid removed by several evaporations to dryness, care being taken to break up all nitrates with hydrochloric acid. Take up with water and a few drops of hydrochloric acid, filter and wash thoroughly. To the filtrate add a slight excess of chlorplatinic acid solution, and evaporate on the steam-bath nearly to dryness so that the salts solidify on cooling. (It is important that the evaporation is not carried to complete dryness as the dry iron and aluminum chlorides are exceedingly difficult to dissolve in acidified alcohol.) To the cooled mass add 15 to 25 cc. of acidified 90 per cent. alcohol, stir, and let stand several minutes, filter, wash with alcohol and ammonium chloride solution and dry in the usual manner. Dissolve the potassium chlorplatinate in hot water, evaporate, dry in water oven for one-half hour, and weigh. The acidulated alcohol is prepared by passing dry hydrochloric acid gas into cool 90 per cent. alcohol until 1 cc. of the alcohol neutralizes about 2.3 cc. of normal alkali.

its applicability to commercial fertilizers I only desire to redirect attention to a most excellent method which has apparently been overlooked.

In Table I are presented the results on 35 samples of soils by

TABLE I.—POTASH IN SOILS.

	Filtered on paper. Acid alcohol.			Filtered on Gooch crucible. Acid alcohol.	
	Official method. Per cent.	Moore method. Per cent.		Official method. Per cent.	Moore method Per cent.
2134	0.39	0.42	2153	0.12	0.13
2135	0.27	0.27	2154	0.10	0.12
2136	0.18	0.18	2155	0.93	0.84
2137	0.52	0.54	2156	0.60	0.63
2138	0.41	0.40	2157	0.85	0.85
2139	0.23	0.24	2158	1.06	1.07
2140	0.14	0.12	2159	0.15	0.16
2141	0.27	0.34	2160	0.18	0.21
2142	0.29	0.27	2161	0.43	0.47
2143	0.29	0.27	....	....	....
Average	0.299	0.305		0.496	0.497
	Plain alcohol.			Plain alcohol.	
2144	0.44	0.42	2162	0.48	0.48
2145	0.48	0.50	2165	0 08	0.09
2146	0.47	0.47	2166	0.38	0.41
2147	0.50	0.48	2168	0.44	0.48
2149	0.44	0.42	2169	0.21	0.21
2150	0.60	0.62	2170	0.21	0.22
2151	0.78	0.82	2171	0.11	0.12
2152	0.67	0.66	2172	0.10	0.11
Average	0.547	0.548		0.25	0.265
General average	0.41	0.41		0.38	0.39

several different procedures. The results are given just as they were obtained in the regular routine of the laboratory; they were not repeated nor rejected. In some cases the differences are larger than they should be between duplicates, but as the average results are practically identical it seems fair to consider such differences as due to the analytical work rather than to the method itself.

The results are not noticeably different where the filtration and washing was done on paper rather than on the Gooch crucible, and under some conditions the use of paper presents certain advantages as the potassium chlorplatinate may be dissolved on the paper in order to separate it from foreign salts, and the solution evaporated, dried and weighed in platinum dishes. The combined

iron and aluminum oxides ranged from 5 to 25 per cent. in these samples. No particular advantage appears to result from the use of the acidified alcohol as recommended by Moore, at least where the amount of lime salts, more especially calcium sulphate, is not large. It would appear, therefore, that the simple method may be further simplified by substituting ordinary 90 per cent. alcohol for the acidified alcohol.

In reviewing the methods used and proposed for estimating potash in fertilizers[1] the writer suggested that the losses now occurring may be partly or entirely overcome by using the method of Moore, provided, of course, any potash is occluded in the ammonia and ammonium oxalate precipitate in the Lindo-Gladding method. The addition of other bases, as proposed by Hare in the lime-water method, appears to be unnecessary except for the purpose of saving the platinum dishes from the effects of igniting phosphates in the presence of organic matter.

In order to determine the applicability of the method to this class of materials several modifications were tried, the purpose of which was to destroy organic matter and ammonium salts in the most expeditious manner. These were destroyed both by aqua regia and by igniting in porcelain dishes, the potash being taken up afterward in distilled water and also in water acidified with hydrochloric acid. In all cases the results have been given corrected and uncorrected for the undissolved foreign salts. In cases where the ignited residue was taken up only in distilled water the impurities in the precipitate were sometimes considerable. Comparisons were also made of washing with plain alcohol and with acidified alcohol. The results are given in Table II.

The samples represented mixtures of the commoner raw materials.

No.	
1759	Acid phosphate and
1761	" " " cottonseed meal.
1762	" " " muriate of potash.
1763	" " " " " " cottonseed meal and nitrate of soda.
2119	Peruvian guano.
2120	Mixed fertilizer.
2911	Acid phosphate and potash salts.
2912	Dissolved animal bone and potash salts.

[1] Proceedings Fifth International Congress of Applied Chemistry, Berlin, 1903.

TABLE II.—POTASH IN FERTILIZERS.

		Moore's Method.								
		Organic matter and NH_3 salts destroyed with HNO_3 + HCl.					Ignited in porcelain.			
		Acid alcohol.		Plain alcohol.			Dissolved in HCl.		Dissolved in H_2O.	
	Official method.	K_2O + undis. salts. Per cent.	Corrected K_2O. Per cent.	K_2O + undis. salts. Per cent.	Corrected K_2O. Per cent.	Filt. on paper corrected. Per cent.	K_2O + undis. salts. Per cent.	Corrected K_2O. Per cent.	K_2O + undis. salts. Per cent.	Corrected K_2O. Per cent.
1759	4.98	5.10	5.01	5.25	5.17	5.31	....	4.96	4.92	4.84
1761	0.92	1.02	0.87	1.37	0.85	0.97	....	1.05	0.81	0.79
1762	0.70	0.68	0.62	0.99	0.67	0.87	....	0.92	1.43	0.79
1763	5.70	6.17	6.13	6.58	6.19	5.85	6.21	6.16	6.13	5.97
2119	3.88	4.00	3.96	3.74	3.71	3.92	3.47	3.44	3.50	3.49
2120	3.60	3.72	3.69	3.82	3.78	3.67	3.83	3.75	3.70	3.68
2911	3.96	4.04	3.99	....	....	....	4.01	3.83	2.09	2.08
2112	4.08	4.14	4.13	....	....	....	4.08	3.93	2.25	2.24

As a rule, the results are slightly higher by the Moore method than by the official method; this is only noticeably so in case of sample 1763. From this it would appear that the flocculent precipitate of iron and lime phosphate has but little to do with the low results usually obtained. It is to be noticed that only when the acid alcohol is used may the impurities contained in the platinum precipitate be neglected. Where plain alcohol is used it is usually necessary to dissolve the potassium chlorplatinate, wash, and reweigh the crucible to obtain the true weight of the potash.

It is obvious that after igniting the material it is not sufficient to treat it with water alone in order to dissolve the potash; such procedure does not always secure all the potash, some of it remaining undissolved, possibly in complex silicates or phosphosilicates, adhering to the dish. It was found that the potash so held could usually be readily recovered by dissolving the ignited material in the dish in dilute hydrochloric acid. This is not always true, however, the potash so held being dissolved but slowly in some instances, and while it appears that all potash may be recovered by prolonged treatment, I do not consider that this method has any advantages over the official method for regular fertilizer work, and further study was abandoned.

LEATHER AND PAPER LABORATORY.

NOTE.

An Explanation.—In the paper in the American *Geologist* on "The Dolomites of Eastern Iowa," which is abstracted in this Journal, **26**, R 373, one fact should have been stated. The author had previously determined that if the silica in these dolomites is in the form of a silicate, it is of a class that can be decomposed by digestion and evaporation with hydrochloric acid. This was ascertained by obtaining concordant results when treating the dolomite powder with a "fusion mixture" of sodium-potassium carbonate, and again by digesting with hydrochloric acid, that is, by evaporating to dryness, stirring until a fine, dry powder results. The residue in each case was treated with pure hydrofluoric and sulphuric acids. Also the residues obtained by dissolving the powder with hydrochloric acid on the one hand, and from digesting with hydrochloric acid on the other, were shown to be silica by the

sulphuric-hydrofluoric method. The fusion process was, therefore, abandoned, partly on account of the difficulty of getting sodium and potassium carbonates free from silica. There is usually only a small amount of silica present in these rocks, often from 0.12 per cent. to 0.75 per cent. The paper referred to further shows that the evaporation to dryness and stirring to a fine powder is not necessary in these analyses, as the same result in silica can be obtained in two or three hours less time by simply dissolving the fine dolomite powder with hydrochloric acid, and considering the undissolved residue as silica, which it really is. This experiment, coupled with the work of the petrological microscope, showed that the silica present is not in the form of a silicate, but in the uncombined condition. The writer has worked with dolomites from various localities, but does not recall an instance where the silicate could not be decomposed by the digestion with hydrochloric acid. This, of course, would not be the case if the silicate consisted of particles of granite, syenite or similar rock.

NICHOLAS KNIGHT.

CORNELL COLLEGE,
October 12, 1904.

REVIEW.

RECENT WORK IN INORGANIC CHEMISTRY.

BY JAS. LEWIS HOWE.

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THE past twelve months have been characterized by an unusually large number of papers in the various journals in the field of inorganic chemistry. These papers are increasingly concerned with the application of the methods and theories of modern physical chemistry to the solution of the problems of inorganic chemistry, or perhaps we should more correctly say that the so-called physical chemistry is being more and more incorporated as an integral part of general chemistry. The result is an almost new inorganic chemistry. Another division of the subject which is beginning to yield important results is that of mixed organic-inorganic compounds, such as "complex" salts with organic acids. The rapid breaking-down of the lines between the different divisions of chemistry progresses, a growing protest against the breaking-up of our chemical societies into those confined to special departments.

During the past year the subject of greatest interest has been

radium and the various problems connected with it. The most important fact which has been presented to chemists for many years is that discovered by Sir William Ramsay (*Proc. Roy. Soc.*, **72**, 204; **73**, 346; *Compt. Rend.*, **138**, 1388) that the emanation given off by radium contains helium. The emanation itself can be condensed by the use of liquid air and is luminous. It has an appreciable vapor pressure and obeys Boyle's law. Judging from its spectrum it appears to be a monatomic gas and for it Ramsay proposes the name of *Exradio*. From the emanation, which has an atomic weight of about 160, helium is given off, 1 gram of radium bromide furnishing in a year 0.0022 mg. of helium. Later, as yet unpublished experiments by Ramsay, indicate that there is also a substance given off from radium which possesses properties very similar to those of lead. If the average life of a radium atom is only 1,100 years, as estimated by Ramsay, a source of radium must be looked for in some atom of higher atomic weight such as uranium, as suggested by Thomson and Rutherford. Boltwood has examined a large number of uranium minerals (*Eng. Min. J.*, **77**, 756; *Am. J. Sci.*, (4) **18**, 97) and finds that the proportion of radium to the uranium present is quite constant. Barker (*Ibid.*, (4) **16**, 161) had already examined a number of thorium minerals which were free from uranium, such as monazite sand from North Carolina, and found a complete absence of radio-activity, and Hofmann and Zerban (*Ber. d. chem. Ges.*, **36**, 3093) examining also thorium minerals, find that their radio-activity is proportional to the uranium they contain. The decay of the radium atom is considered at length from a theoretical standpoint by McCoy (*Ibid.*, **37**, 2641). He finds it probable that the successive decomposition products are as follows: $Ur \rightarrow UrX \rightarrow Ra \rightarrow RaEm \rightarrow EmX \rightarrow He$. Since the decay of UrX, RaEm and EmX is very rapid, their quantity in proportion to that of radium is very small. The amount of helium in uranium ores is not proportional to the amount of uranium on account of its diffusibility; the amount of radium is about $^1/_{300,000}$ part of the content of uranium. The experimental results of McCoy agree with those of Boltwood.

The spark spectrum of radium has been carefully studied by Runge and Precht (*Sitzungsber. Akad. Wiss.*, Berlin, **1904**, p. 417; *Ann der Phys.* (4) **14**, 418) and its character found to be that of an alkaline earth metal, while Crookes (*Proc. Roy. Soc.* **72**, 295) has photographed the ultra-violet spectrum, and his photographs are reproduced in his paper. The electrical conductivity of radium bromide solutions has been found by Kohlrausch and Henning (*Verh. d. phys. Ges.*, **6**, 144) to be very similar to that of barium, neither the high atomic weight nor the ionizing influence of radium having any especial effect upon its electrical conductivity. The calorific effect of radium has been further studied by Rutherford and Barnes (*Phil. Mag.* (6), **7**, 202), and by

Precht (*Verh. d. phys. Ges.*, **6**, 101). The former find the evolution of heat rather more than 100 cal. per hour per gram of radium. After expelling the emanation of radium by heat and condensing the emanation by liquid air they find that the radium and the emanation give complementary time curves. Seventy-five per cent. of the evolution of heat is to be attributed to the emanation and its decomposition products. The heat activity of radium, which has lost its emanation, gradually increases, while that of the emanation gradually decreases. The conclusion is drawn that the evolution of heat is a phenomenon which accompanies the successive transformations of radium. Precht, using three different methods and different radium preparations, obtains results which agree very closely (113.3 cal. per hour) and considers that the heat evolution of radium probably has the significance of a physical constant.

F. Rinne has examined (*Centrbl. f. Min. u. Geol.*, **1903**, p. 134) radium bromide from a crystallographical standpoint and finds that it resembles in every respect the corresponding barium salt, so that he places the element chemically, spectroscopically, and crystallographically in the magnesium, calcium, strontium, barium group. Others also have confirmed this conclusion. The rapidity with which the stains caused by radium on glass disappear is found by Georgiewsky (*J. Russ. Phys. Chem. Soc.*, **36**, 1) to increase with the temperature, but they also disappear very slowly at ordinary temperature. The same is true of the more slowly formed spots on quartz. Mica is superficially colored, while gypsum and Iceland spar are not colored at all. All these minerals are, however, affected in their optical properties, which Georgiewsky thinks is due to a dissociation. A thin sheet of aluminum was found by Orloff (*Ibid.*, **36**, 41) after several months' exposure to radium bromide, to be covered with little drops which appeared to be melted metal. These drops were radio-active and retained this activity unchanged after washing, boiling with water, heating to 320°, and even after keeping for seven months. Crookes (*Proc. Roy. Soc.*, **74**, 47) finds that diamonds are hardly affected by the β-rays of radium, but on embedding in radium bromide are colored dark on the surface. This layer of color was removed by the nitric acid-potassium chlorate mixture, but the whole mass of the diamond previously of yellowish tint, had become faintly bluish-green.

Regarding the other supposed radio-active elements, although much work has been put upon them the past year, notably by Marckwald, Debierne, Hofmann, Zerban, von Lerch and others, no definite results seem to have been obtained and much confusion still exists. Pellini (*Gazz. chim ital.*, **33**, ii, 35) suggests that the anomalous high atomic weight of tel-

lurium is probably due to the presence of a small admixture of a radio-active element closely resembling tellurium, with an atomic weight of about 212, which it has been thus far impossible to isolate from tellurium.

Both Grüne (*Ber. d. chem. Ges.*, **37**, 3076) and Hofmann (*Ibid.*, **37**, 3407) have been able to prepare very strongly phosphorescing zinc blende by the addition of minute quantities of other elements to the zinc solution before precipitation with hydrogen sulphide. Grüne obtains the best results by using copper, while Hofmann uses magnesium in the presence of common salt. Both obtain striking results with manganese.

The electrical conductivity of non-aqueous solutions continues to attract some attention—not as much as it deserves—but no generalizations have as yet been reached, nor indeed any approach to them. Plotnikoff (*Ztschr. phys. Chem.*, **48**, 220) has studied bromine as a solvent. Its solutions of the bromides of aluminum, arsenic, tin and sulphur are not conductors. Its solutions of the bromides of phosphorus and of antimony conduct, as well as those of the double compounds of aluminum bromide, with carbon bisulphide and ethyl bromide. In general the specific conductivity increases with concentration. In all these cases complex compounds seem to be formed and according to Plotnikoff the formation or presence of complex compounds appears to be the condition of conductivity. McIntosh, Walker and others (*Proc. Roy. Soc.*, **73**, 450, 454; *J. Chem. Soc.* (Lond.), **85**, 1082, 1098, 1106) have worked with the liquid hydrogen compounds, HCl, HBr, HI, H_2S, and H_3P, and also with organic solvents. The hydrogen compounds dissolve mere traces of metallic salts, but many organic substances are readily dissolved, such as amines, amides, nitriles, alcohols, ketones, ethers, acids and esters. In every case where a conducting solution is formed, the solute contains an element which is capable of assuming a higher valence. Walker holds that so far from being a prerequisite of chemical action, ionization is to be looked upon as a generally necessary result of chemical action. Like Plotnikoff, he considers that the non-ionizing solvents become conductors only through reaction with the solute. The whole subject of the reactions of salts in non-aqueous solutions is being exhaustively studied by Naumann and his pupils (*Ber. d. chem. Ges.*, **37**, 3605, 4328).

The question as to whether magnetism is capable of influencing chemical reactions has been taken up again, this time by Schweitzer (*Phys. Ztschr.*, **4**, 852), and a series of experiments carried out on both silver and iron salts by the aid of a powerful electro-magnet. The silver halogen salts were used in the form of gelatine emulsion plates and of the iron salts the ferric oxalates and tartrate were studied in solution. In no case were any changes discoverable in

the magnetic field nor were the photochemical reactions accelerated or retarded.

A considerable amount of work has been done by Euler (*Ber. d. chem. Ges.*, **36**, 2878, 3400; **37**, 2391; *Arkiv. för Kemi, Min. och Geol.*, **1903**, i, 77) on the constitution of complex ions, particularly those containing silver, zinc and cadmium, and also on the change of trivalent nitrogen into quinquivalent. The latter he attempts to handle in a quantitative manner, based on the theory of electrolytic dissociation and the law of mass action. For the equilibrium of ammonia in aqueous solution he proposes the following equation, $k = \frac{K_{H_2O}}{K_2 \cdot K'_2}$, where K_2 and K'_2 are the following constants, $C^{+}_{NH_4} \cdot C^{-}_{OH} = K_2 \cdot C_{NH_4OH}$ and $C^{-}_{NH_3} \cdot C^{+}_{H} = K'_2 \cdot C^{+}_{NH_4}$. Here the assumption is made that the nitrogen atom can take up positive as well as negative charges, but this is only the expression of the fact that the nitrogen atom can unite with four positive and one negative atom to form a stable compound. Euler applies the same principle to other cases of variable valence. He also takes the position that the composition of all chemical compounds and molecular compounds is to be conceived of simply as a function of a valence force ("Valenzkraft") which is probably of an electrical nature, and also, according to van't Hoff, a function of the temperature, the pressure, and sometimes of the solvent. In his last paper, discussing certain platinum bases, he holds that as far as regards its basicity ammonia can play a passive rôle, just as water can at times be basic and not basic. A somewhat different mathematical treatment of complex compounds and ions is given by Bodländer (*Ber. d. chem Ges.*, **36**, 3933), in which he makes use of what he calls ergochemical decomposition equations.

Cain (*Chem. News*, **90**, 39, 52) considers that in ammonium compounds the fourth hydrogen atom is not attached to the nitrogen and would express the hydroxide and chloride by the formulas $H_2N{=}OH_2$ and $H_3N{=}ClH$, the chlorine being trivalent and the oxygen quadrivalent. In ammonium sulphate the fourth hydrogen atoms are attached to the oxygen atoms which are here also quadrivalent. A similar reasoning is extended to the more complex ammonia compounds and used also as an explanation of the isomerism in one of these compounds. The subject is also treated by LeBel (*J. Chim. Phys.*, **2**, 340) from a stereomeric standpoint.

Some little work has been done upon other complex salts, but here again far less than the subject deserves. Smith has continued his researches (this Journal, **25**, 1223, 1227, 1229) upon the complex tungstic acids, preparing ammonium vanadico-phosphotungstates containing silicon, titanium, zirconium, thorium, and bivalent tin. He has also prepared ammonium vanadium tungstates in which the vanadium is in the V_2O_3 form and those in which the

vanadium is represented by V_2O_4. Again he has prepared a series of complex tungstates with Al_2O_3, Fe_2O_3, Cr_2O_3, Ni_2O_3, Mn_2O_3, and Bi_2O_3. The aluminotungstates are very stable, and the bismuthotungstates separate as a yellow oil, which can be brought to crystallization. Kehrmann (*Ztschr. anorg. Chem.*, **39**, 98) has investigated more fully the silicotungstates and finds that the composition of Marignac's potassium salt should be $7K_2O.2SiO_2.20WO_3$. While Smith's manganese tungstates appear to contain Mn_2O_3, Just (*Ber. d. chem. Ges.*, **36**, 3619), working in the presence of sodium persulphate, has obtained a manganese tungstate containing MnO_2, to which he gives the formula $Mn(WO_4Na)_4.Na_2WO_4.18H_2O$. He also has prepared complex salts in a similar way containing manganese and polytungstic acid, as well as metatungstic acid. Some attention has been paid to the complex salts with organic acids, Grossmann (*Ztschr. anorg. Chem.*, **41**, 43) having studied the molybdo-oxalates as well as tungsto-tartrates and citrates, especially with reference to their electrical conductivity. Mandel (*Ibid.*, **37**, 252) has examined quite a large series of complex salts of zirconium with organic acids. In the case of acids with hydroxyl groups attached to adjacent carbon atoms, as tartaric acid, he considers that the zirconium replaces the hydrogen of the hydroxyls.

Following out the work of Werner, Pfeiffer (*Ber. d. chem. Ges.*, **37**, 4255) has begun a series of researches upon the stereochemistry of chromium, basing his theories largely upon the study of the ethylene diamine bases. The work thus far prosecuted in every way substantiates the results which Werner has obtained with the platinum bases.

According to Werner, the compound $Pt(PCl_3)_2Cl_2$ is to be considered as analogous to $Pt(NH_3)_2Cl_2$, but the compound $Pt(PCl_3)Cl_2$ has no analogue in the ammonia series. Rosenheim (*Ibid.*, **37**, 394), from a study of the ethyl ester of phosphorous acid, concludes that the conjecture of Werner is correct. In the case of $Pt(PCl_2)Cl_2$ the platinum would seem to have a coördination number of four, but in the derivative ethyl ester compound molecular weight determinations, both by freezing and by boiling point in benzene, show that the formula must be doubled, so that it is probable that the formula of the chloride should be $PCl_3.Cl_2.Pt.Pt.Cl_2.PCl_3$. Oxidation with chlorine and bromine gave rise to platini-compounds of phosphoric ethers which form beautiful purple crystals. He also describes in the paper the preparation of pure $PtCl_4$ by heating dry chlorplatinic acid in chlorine at 275° in a diphenylamine bath, a method which gives excellent results.

Passing to a consideration of the elements and their simpler compounds, Tutten has continued his work on the relations that exist between the metals of the alkalies in their compounds and extended it to ammonium (*J. Chem. Soc.* (Lond.), **83**, 1049).

Taking up ammonium sulphate and its constants he finds that in nine properties, which include solubility, molecular volume, and optical properties, ammonium lies between rubidium and cesium and nearer to the former. In some respects it stands slightly nearer cesium. He thinks it remarkable that the replacement of potassium by a group of five atoms should have less effect upon the molecule than its replacement by the single cesium atom. It is his view that either the atoms in the molecule have sufficient space at their disposal for the replacement of two atoms by ten without appreciably affecting the external dimensions of the molecule, or else the free space between the molecules must be sufficiently great for the addition of eight atoms to the molecule without increasing the distance between the centers of adjacent molecules. The possibility of atomic compression does not seem to be considered by him.

Two papers by Haber (*Ztschr. anorg. Chem.*, **38**, 377; **40**, 465), on glucinum, have appeared. In the first he gives the explanation of the discrepancies existing in the descriptions of glucinum hydroxide. He finds that it exists in two forms. When first precipitated by alkalies it is voluminous, absorbs carbon dioxide, and is easily soluble in potassium hydroxide and carbonate, in ammonium carbonate and acids. It gradually goes over into a more stable form in which it is granular, less affected by carbon dioxide and insoluble in potassium carbonate, dilute alkalies and dilute acids. In this condition it is rapidly dissolved by hot deka-normal potassium hydroxide. In the second paper he calls attention to the fact that if glucinum hydroxide is dissolved in glacial acetic acid, it can be, to a very large extent (about 90 per cent.), extracted by shaking with chloroform. This affords an easy separation from iron and aluminum. The solution of ferric hydroxide in acetic acid is also soluble in chloroform, but is not extracted by chloroform from the aqueous solution. Tanatar (*J. Russ. Phys.-Chem. Soc.*, **36**, 82) has repeated the work of Lacombe and Urbain (*Compt. Rend.*, **133**, 874; **134**, 772 (1902)) on the basic acetate of glucinum, and from this and his own investigations he comes to the conclusion that glucinum is probably a quadrivalent element with an atomic weight of 18.2. It will be recalled that Lacombe and Urbain drew the conclusion from their work that the ordinary view held of glucinum as a bivalent element is correct. Parsons (this Journal, **26**, 721) has made a study of this basic acetate and used it for the determination of the atomic weight of glucinum, and he has also used the glucinum acetonylacetonate for the same purpose.

Baud has continued his researches on aluminum compounds (*Compt. Rend.*, **137**, 492; *Ann. chim. phys.* (8), **1**, 8), particularly on the double compounds of the chloride. He had already prepared compounds with NH_3 (four in number), H_2S, and C_2H_2. He now finds two compounds with SO_2,—$Al_2Cl_6.2SO_2$ and Al_2Cl_6.

SO_2,—and also prepares calcium, strontium, barium and zinc salts of the type $2Al_2Cl_6.3MCl_2$. A salt which separates from the hot, rather strongly acid solution of the sulphate, he finds to be $Al_2O_3.4SO_3.4H_2O$. This is soluble only with difficulty in water.

From determinations of the specific heat Sachs (*Ztschr. f. Krist.*, **38**, 495) concludes that indium is trivalent and belongs to the aluminum group. The same is indicated by octahedra appearing in the metal as obtained electrolytically. Besides determining the atomic weight, Thiel (*Ber. d. chem. Ges.*, **37**, 175; *Ztschr. anorg. Chem.*, **40**, 280) has prepared several new salts, including the sulphides In_2S_3 and In_2S.

Many papers have appeared upon the subject of the rare earths and while some progress has been made, the solution of the problem of their nature seems as far as ever from attainment. Benedicks (*Ztschr. anorg. Chem.*, **39**, 41), from a study of the atomic volumes of these elements, favors the suggestion of Brauner that these elements, as a group, take their place in the third and fourth groups between barium and tantalum, and that no maximum in the atomic volume curve occurs in this space. This would eliminate two of the horizontal rows of the Mendeléeff table of the periodic system. This is what has been called the asteroid theory of the rare earths, and it comes much nearer expressing the facts in the case than any other theory which has been proposed. One of the more important pieces of work which has been done upon the rare earths is the solution by Brauner (*Ibid.*, **38**, 322; **39**, 261) of the problem of the sulphates of cerium, and in particular the determination of the constitution of the puzzling cero-ceric sulphate. He finds that ceric sulphate, $Ce(SO_4)_2$, forms a complex acid with sulphuric acid (hypothetically $H_4Ce(SO_4)_4$) which forms, with certain trivalent elements, acid salts, the constitution of the cerium salt being $Ce'''HCe''''(SO_4)_4.12H_2O$. This is the cero-ceric sulphate. In addition to this Brauner prepared the lanthanum, praseodymium, and neodymium salts of this cerisulphuric acid. He has also prepared the acid sulphates of trivalent cerium, lanthanum, praseodymium, neodymium, samarium, and yttrium. The cerium salt has the formula $H_3Ce(SO_4)_3$ and should be considered as cero-sulphuric acid. The sulphates of the other metals are analogous. Sterba (*Ann. chim. phys.* (8), **2**, 193) has continued his work on cerium, attempting to prepare pure cerous oxide, CeO, by heating the oxalate in a vacuum, or reducing ceric oxide with hydrogen or zinc. While some of the desired product is obtained, it is always contaminated with the higher oxide. Baskerville (this Journal, **26**, 46, 54, 71, 67, 75) has examined the various methods of purifying praseodymium and neodymium. For the former he finds the best to be the heating of a saturated solution of citric acid in which impure praseodymium hydroxide is dissolved. Neodymium he precipitates fractionally

with hydrochloric acid gas. His attempts to prepare alums of these earths and of lanthanum were unsuccessful, but a number of new double sulphates were obtained. These contained in no case more than four molecules of water of crystallization. He has also obtained several lanthanates of the alkalies and of barium. Biltz (*Ann. Chem.* (Liebig), **331**, 334) has prepared and studied the acetonylacetonates of the rare earths, which are well characterized compounds. He hoped to find the thorium compound well suited for atomic weight determination, but the difficulties were unsurmountable. By fractional crystallization of the magnesium double nitrates in the presence of bismuth Urbain and Lacombe (*Compt. Rend.*, **137**, 792; **138**, 84, 1166) resolved the gadolinium-samarium group and have prepared a considerable quantity of samarium for atomic weight determinations. Large quantities of the earths were fractioned by Muthmann (*Ann. Chem.* (Liebig), **331**, 1, 46, 58, 60) by the magnesium double nitrate method and by the electrolysis of the fused chlorides, the free metals obtained and their properties studied. Various alloys were made, as well as the hydride and nitrides of praseo- and neodymium. The best means of separation of the rare earths is found by R. J. Meyer (*Ztschr. anorg. Chem.*, **41**, 97) to be the potassium double carbonates, and he has studied several series of alkali double carbonates. Baskerville (this Journal, **26**, 922) has further investigated the products obtained by fractioning thoria with carbon in a current of chlorine, isolating a more volatile chloride, and a non-volatile unchanged oxide, while the greater portion distils at a high temperature as true thorium tetrachloride. The more volatile chloride is of a new element, berzelium, with an atomic weight of 212, while the element forming the non-volatile oxide is also new, and named carolinium. Its atomic weight is 255.6. The purified thorium shows an atomic weight of 220.6, or decidedly lower than that of the old thorium. Baskerville deems the elementary nature of berzelium and carolinium as probable, though not yet confirmed spectroscopically. While these are perhaps the more important researches upon the rare earths there have been many other papers on the subject, and it is evident that this difficult field is attracting more and more attention.

During the past year Moissan (*Compt. Rend.*, **137**, 292; **138**, 1558) has described two new carbides from his electric furnace The first of these is a double carbide of chromium and tungsten. This may be prepared either from the elements or from the oxides. It is very resistant to reagents and scratches the ruby but not the diamond. The other of these products is a new carbide of molybdenum. It is prepared from the metal and carbon in the presence of aluminum. A lower current and shorter heating are used than in making the carbide Mo_2C. The new carbide has the formula

MoC, analogous to that of tungsten and is very resistant to reagents. Moissan thinks that this carbide in the form of a double carbide is present in molybdenum steel. Moissan (*Ibid.*, **138**, 1299) has also determined the solubility of silicon in silver, which increases very rapidly with the temperature and is over 40 per cent. at 1470°. A portion of the silicon which crystallizes out is a new modification of the element, soluble in hydrofluoric acid. Dufour (*Ibid.*, **138**, 1040, 1101, 1169) finds that at a temperature above the fusion point of silicon this element unites with hydrogen to form SiH_4 in very small quantities. SiO_2 is also reduced by hydrogen at a similar high temperature, as can be shown by passing hydrogen through a quartz tube heated in an oxygen blowpipe. The apparent volatility of silicon in a Geissler tube in the presence of SiH_4 is really due to the successive decomposition and recomposition of the SiH_4 and is not a true volatilization. Quite a number of interesting compounds of silicon have been prepared by Blix (*Ber. d. chem Ges.*, **36**, 4218, 4220), analogous to carbon compounds. Among these are silicon sulphobromide, $SiSBr_2$, and silicon thiourea, $SiS(NH_2)_2$. The latter is a white amorphous powder which only slowly decomposes in the air. He has also prepared silicon imide, $Si(NH)_2$; silicam, Si_2N_3H; and silicon nitride, Si_3N_4. The silicam, which is an indifferent powder, unacted upon by water, is prepared by heating the imide in nitrogen to 900°, and by heating to 1200° it is itself converted into the nitride. The analogous titanium amide, $Ti(NH_2)_2$, was also obtained.

A boron imide, $B_2(NH)_3$, is formed by Joannis (*Compt. Rend.*, 139, 364) by the action of ammonia on boron bromide at low temperature. Using phosphorus trichloride at —78°, a mixture of phosphorus amide and imide, or more probably a mixed amide-imide, $NH.P.NH_2$, is observed, which above zero begins to decompose into phosphorus imide.

To the very small number of double nitrates known, Wallbridge (*Am. Chem. J.*, **30**, 154) has added a double nitrate of potassium and barium which has the composition $K_2Ba(NO_3)_4$. Groschuff (*Ber. d. chem. Ges.*, **37**, 1486; *Ztschr. anorg. Chem.*, **40**, 1) finds that series of acid nitrates and the alkalies exist of definite composition, as $KNO_3.HNO_3$ and $KNO_3.2HNO_3$. He compares the latter to KOH.2HOH.

The effect of light upon the oxidation of metallic arsenic has been tested by Panzer (*Verh. Vers. d. Ntf. u. Aerzte*, **1902**, ii, 79), who exposed arsenic mirrors obtained by Marsh's process, under different conditions. In the dark no change took place even in the presence of moisture, but in the sunlight the mirrors disappeared within a few days. The product formed was chiefly As_2O_3. Cooke (*Proc. Chem Soc.*, **19**, 243) has tested the action of water and of

caustic soda upon metallic arsenic, both in the crystalline and amorphous forms. The action of water on the latter is very slight, but the alkali acts somewhat more strongly, especially when concentrated. The presence or absence of air seems to be without effect. Water and caustic soda are practically without action on crystalline arsenic in the absence of the air, but have some effect when air is present. Dilute alkali has no more effect than water alone. In all cases the arsenic goes into solution as As_2O_3, and in no instance was arsine observed. Stock and Guttmann (*Ber. d. chem. Ges.*, **37**, 885, 901, 1957) have continued their work on stibine, and described in full its chemical and physical properties. Its decomposition, which may take place explosively, is studied from the standpoint of physical chemistry. Its physiological action was investigated and it was found to be even more poisonous than arsine. When decomposed by oxygen at —90° the yellow modification of antimony is formed very sparingly, and goes over into the black modification at —50° in a few seconds. The work of Koppel on quadrivalent vanadium, which was made note of last year, has been extended to the double oxalates and thiocyanates. The latter salts, of which $K_2VO(CNS)_4$ may be taken as a type, are peculiar in that they crystallize with five molecules of water. The sulphates, double oxalates, and halides of trivalent vanadium are obtained by Bültemann (*Ztschr. Elektrochem.*, **10**, 141) by the electrolytic reduction of vanadates. The alums, previously prepared by Piccini, are dimorphous, existing in a red and in a blue modification. They are convertible, one into the other, by recrystallization, and have the same composition.

Stähler (*Ber. d. chem. Ges.*, **37**, 4405, 4411) finds that in analogy with chromium the violet titanium trichloride is converted by boiling with hydrochloric acid and alcohol into a green modification. This could not be isolated, but the double rubidium and cesium salts were obtained, of the formula $Rb_2TiCl_5.H_2O$. The corresponding vanadium salt, $Rb_2VCl_5.H_2O$, was also prepared. The water appears to be an integral part of the molecule, replacing a chlorine atom. There is here an analogy with the violet-red chromium chloride series, $M_2CrCl_5.H_2O$, of Neumann (*Ann. Chem.* (Liebig) **244**, 329) and the aquo chlorruthenate series, $M_2RuCl_5.H_2O$, of Howe. In the latter case also the conversion of the ordinary chloride into the aquo salt is by boiling with hydrochloric acid and alcohol.

Cryoscopic studies of the different modifications of sulphur in different solvents have been made by Popoff and by Timofejeff (*J. Russ. Phys.-Chem. Soc.*, **35**, 642, 644). In dimethylaniline and benzene the association of all three modifications is proportional to the concentration, being at a dilution of 0.5 per cent., equivalent to S_6. By the boiling-point method the molecular

weight of rhombic sulphur corresponds to S_6 in chloroform, to S_8 in carbon bisulphide, while in benzene the value varies from S_5 to S_{10}. Gosio has continued his work on the reducing action of certain micro-organisms, and extended it to tellurium and selenium salts (*Atti. Accad. Lincei*, Rome, (5) **13** i, 422, 642). Tellurates are reduced within two or three minutes by *Hyphomycetes*, while fifteen to twenty minutes are required for arsenic compounds. Selenites are reduced more slowly. It is suggested that this bio-chemical reaction can be utilized to determine the viability of certain micro-organisms. Gutbier has suggested a new method for preparing telluric acid (*Ztschr. anorg. Chem.*, **40**, 260), which is an improvement upon the chromic acid method in so far that it yields a purer product. It consists in dissolving the tellurium dioxide in warm caustic soda or potash, and then oxidizing with 15 per cent. hydrogen peroxide. The telluric acid can then be precipitated by nitric acid.

Double chromates with six molecules of water, corresponding to the double sulphates, have at last been prepared. Briggs (*J. Chem. Soc.* (Lond.), **85**, 677) has described several members of the nickel and the magnesium series. He has also prepared a number of the double chromates, as well as the double molybdates crystallizing with ammonia (two molecules). This work of Briggs affords some hope that chromate alums may yet be forthcoming. Working in the same direction as Briggs, Gröger (*Monatsh. Chem.*, **24**, 483; **25**, 520) obtains much more complex compounds, apparently due to his working at a higher temperature than Briggs. By the action of hydrogen peroxide on chromium hydroxide in the presence of ammonia, Hofmann (*Ber. d. chem. Ges.*, **37**, 1663, 3405) obtains a salt of the composition $O_2Cr(OONH_4)_2$, to which he gives the name of "chromatodipersaures Ammonium." On treatment with dilute acetic acid the acid salt $O_2Cr(OONH_4)(OOH)$ is formed. The corresponding silver salt is relatively stable. These salts lose oxygen readily, going over into the chromates. With sulphuric acid in the presence of ether, the familiar blue solution of perchromic acid, $HCrO_5$, is obtained.

By electrolytic reduction Chilesotti (*Atti. Accad. Lincei*, Rome (5), **12** ii, 22) obtains from molybdic acid in hydrochloric acid solution, a solution of trivalent molybdenum, from which double salts can be prepared. The potassium salt has the formula K_3MoCl_6, while the other alkali salts belong to the type $M_2MoCl_5.H_2O$, possibly of the same nature as the aquo salts. Engels (*Ztschr. anorg. Chem.*, **37**, 125), continuing the work of V. Knorre on the tungsten bronzes of sodium and potassium, has prepared a series of these bronzes containing barium, strontium and calcium. The tungstates of the alkalies have also been further investigated by Schaefer (*Ibid.*, **38**, 142).

Ruff and Plato (*Ber. d. chem. Ges.*, **37**, 673) have overcome decided experimental difficulties in preparing the fluorides of titanium, tin, and antimony, by the reaction between the chlorides and hydrofluoric acid. The acid is obtained as a perfectly dry liquid by heating potassium hydrogen fluoride; the chloride of the reacting element is added directly to it and the mixture, after standing, fractionally distilled. The physical constants of the fluorides were also obtained. For the preparation of anhydrous chlorides Matignon and Bourion (*Compt. Rend.*, **138**, 631, 760) heat the oxide in a current of chlorine and sulphur chloride. If the chloride is difficultly volatile an excess of the chloride of sulphur is used; if volatile, an excess is avoided. In this way they have prepared $SiCl_4$, $2AlCl_3.SCl_4$, $ThCl_4$, $VOCl_3$, VCl_4, WO_2Cl_2, $WOCl_4$, as well as chlorides of praseodymium, neodymium, samarium, chromium, nickel, iron, and cobalt. Oxides, as well sulphates, carbonates and other oxygen salts of most of the metals can be converted into chlorides. It is thus a method of general application. A paper which has filled out something of a gap in our chemical knowledge is by Hendrixson (this Journal, **26**, 747) on the action of metals on chloric acid. In some cases hydrogen is evolved and in most cases at least a part of the chloric acid is reduced to hydrochloric acid. This acid shows no tendency to react with the chloric acid, as there is in no instance a production of chlorine nor were any of the lower oxides or acids of chlorine found. Defacqz (*Ann. chim. phys.* (8), **1**, 337) has utilized the reaction between manganese fluoride and the halide salts of other metals to prepare fluorides and fluo-halides. Fluo-chlorides, fluo-bromides and fluo-iodides of the alkaline earth metals have been prepared as crystalline powders and the specific gravity of each has been determined. All have a formula analogous to $CaF_2.CaCl_2$.

From the fact that gold in nature is frequently accompanied by fluor spar, it would seem possible that a fluoride of gold might have played a part in the mineralization of veins. Lenher (this Journal, **25**, 1136) has, therefore, tried many different methods to prepare a compound of fluorine and gold, but without success. He, however, calls attention to the fact that a number of years ago Moissan obtained, by the action of fluorine on gold at red heat, a yellow hygroscopic substance which decomposed easily into fluorine and gold. Some time ago Lenher showed that gold was soluble in selenic acid and in a solution of telluric acid in sulphuric or phosphoric acid. This solution might be caused by the splitting-off of oxygen in the nascent state, so Lenher (*Ibid.*, **26**, 550) tried to effect the solution of gold by the use of sulphuric acid in presence of oxidizing agents such as MnO_2, Pb_3O_4, etc. Under these conditions gold was found soluble, easily when heated, but to some extent even at zero. In most cases phosphoric acid can be sub-

stituted for sulphuric. Berthelot (*Compt. Rend.*, **138**, 1297) finds that both platinum and gold are, to some extent, acted on by fuming hydrochloric acid in the light, especially where there is present a trace of some substance such as $MnCl_2$, which can be further oxidized in the air. In complete darkness this action does not take place even when $MnCl_2$ is present. Quite an extensive study of the oxides of platinum has been made by Wöhler (*Ber. d. chem. Ges.*, **36**, 3475; *Ztschr. anorg. Chem.*, **40**, 423). Platinum has generally been classed as a metal which will not unite with oxygen directly at any temperature. Wöhler finds, however, that under circumstances it may be oxidized. The activity of platinum black seems to be in part due to the presence of an oxide and hydroxide of bivalent platinum. This oxide is very stable and begins to give up its oxygen only at 392°, being completely decomposed at 431°. Wöhler obtains the hexaoxyplatinic acid, $Pt(OH)_6H_2$, by boiling chlorplatinic acid with excess of caustic soda and precipitating in the cold with acetic acid. Belluci (*Atti Accad. Lincei*, Rome, (5), **12** ii, 635) had already independently identified the hydrated oxide, $PtO_2.4H_2O$, of Topsoë as being the hexaoxyplatinic acid, and had prepared several of its salts. The only member of the chlorplatinic acid series remaining unknown is the trichlorplatinic acid, $PtCl_3(OH)_3H_2$.

Moissan (*Compt. Rend.*, **137**, 229), by heating in the electric furnace a mixture of ruthenium and crystallized silicon, has prepared a ruthenium silicide, RuSi, which he describes as a very hard and exceedingly resistant body. It is peculiar in being the only known compound of ruthenium which is not attacked by potassium hypochlorite. Lind (this Journal, **25**, 928) has submitted potassium nitrosochlorruthenate to an examination from the standpoint of physical chemistry, and finds its behavior to be very much like that of the chlorplatinate. The nitrosochlorruthenates are the only class of halide compounds of ruthenium which form stable solutions. Howe (*Ibid*, **26**, 543) has described the preparation of the chlorruthenates, M_2RuCl_6, and the aquochlorruthenates, $M_2Ru(OH_2)Cl_5$, and also of the bromruthenites, bromruthenates and aquobromruthenates. The chlorruthenates could be formed only by the action of chlorine upon the aquochlorruthenates, though Antony has prepared a potassium chlorruthenate by the action of HCl on K_2RuO_4.

A large amount of interesting work has been done upon colloidal solutions, and this bids fair to attract more attention as time goes on. A rather new line of investigation has been opened up by Hausmann (*Ztschr. anorg. Chem.*, **40**, 110) on the formation of precipitates in jellies. It had been noticed by Liesegang in the case of silver nitrate and ammonium bichromate that the precipitate appeared in layers, and Hausmann finds that this is gen-

erally the case. A number of interesting problems are suggested by this line of work.

Finally mention may be made of the determination of the specific gravity of liquid and solid oxygen, nitrogen and hydrogen at very low temperatures by Dewar (*Proc. Roy. Soc.*, **73**, 251), and of the determination of the compressibility of these same gases and of carbon monoxide, between one-half and one atmosphere pressure, by Lord Rayleigh (*Ibid.*, **73**, 153). Calculated from these results the atomic weight of nitrogen becomes 14.003, which differs from the generally accepted atomic weight, 14.04, by an amount greater than can be accounted for by experimental errors. The cause of this discrepancy remains to be explained.

NEW BOOKS.

THE PURIN BODIES OF FOOD STUFFS. By I. WALKER HALL, M.D., Owens College, England. Philadelphia: P. Blakiston's Son & Co. 1904. xiii + 201 pp. Price, $1.50.

The book under consideration is a revision of the author's first edition of "Purine Bodies." It has been reissued, as the author states in his preface, to meet a popular demand. Several portions of the first edition have been rewritten, and the results of recent investigations included.

The greater part of the book is devoted to investigations undertaken by the author to obtain information as to the physiological action of purine bodies and their metabolism. The author has made estimations of the purine bodies present in the common foodstuffs, and studied their effects upon the metabolic processes in animals and man when introduced into the body subcutaneously or taken by the mouth.

A chapter on the action of drugs upon purine excretion is introduced, and an index and tables of analytical methods are appended.

A commendable feature of the work is the completeness of the literature references. The book is well written and remarkably free from typographical errors. The book should be of interest to all who are interested in physiological chemistry.

TREAT B. JOHNSON.

AN ATTEMPT TOWARDS A CHEMICAL CONCEPTION OF THE ETHER. BY PROFESSOR D. MENDELÉEFF. London : Longmans, Green and Co.

The author believes that a real conception of the ether cannot be obtained without recognizing its chemical nature as an elementary substance, and that no elementary substance is conceivable which is not subject to the periodic law. The idea of the division of atoms into electrons seems to him to proceed from a lack of definite notions about the chemism of the ether. The phenomena of radio-activity have given him courage to speak while clearly seeing the risk incurred in so doing.

Since the ether pervades all matter, its atoms must have less mass and greater velocity than those of hydrogen. What is even more important, they must have less capacity than even those of hydrogen, to form compounds with the bodies which they permeate. The author therefore supposes that the ether is a very light gas belonging to the argon group, the group having zero affinity. Since the ether pervades all space without being imprisoned in the atmosphere of stars which may perhaps have masses fifty times as large as that of our sun, he thinks its molecular velocity not less than 2,250 kilometers a second. With this velocity, the atomic mass is some such quantity as one millionth that of hydrogen.

While the atoms of the ether do not *combine* with others, they may nevertheless accumulate around large centers of attraction, such as the sun, among heavenly bodies, or such as the atoms of uranium, thorium, or radium, in the world of atoms. The entrance or exit of such atoms of ether would exhibit peculiar phenomena; such conceptions of the ether give means, if not of analyzing these phenomena, at least of understanding their possibility.

To the opinions just cited, Mendeléeff adds the declaration that he makes no attempt to solve the numerous problems suggested, the majority of which he characterizes as unfathomable. The pamphlet is a dignified attempt to secure that certain conceptions, which were suggested to him by facts, shall not pass away without a chance for their elaboration and correction, if they contain truth; without saving others from repeating them, if they are proved to be false in their basis. Since we cannot deny the substantiality of the ether, a search for its chemical nature seems to Mendeléeff to

be required, and the object of his tentative answer is, to bring this primary question to the fore. EDWARD W. MORLEY.

THE STUDY OF THE ATOM. BY F. P. VENABLE. Easton, Pa.: The Chemical Publishing Company, 1904. vi + 290 pp. Cloth. Price, $2.00, net.

This book appears to be an attempt to give a semi-popular account of the history, nature, and behavior of atoms. The opening chapters (75 pp.) deal with: "Ancient Views as to the Nature of Matter" and the atomic theory "from the Greek Philosophers to Dalton," and contain a résumé of the speculations on this subject. Then follows an account of the employment of the atomic theory by Dalton (34 pp.) and the advances which culminated in the adoption, at the suggestion of Cannizzaro (1858), of the criteria still used for determining atomic weights (43 pp.). On the ground that "The discovery of this Natural System has done so much to make clearer the nature of the atom * * * ," the next chapter deals with the Periodic System (30 pp.). In Chapter VI, "Affinity, the Atomic Binding Force," the various views as to the nature of "the attraction between atom and atom" and the various methods of measuring it are discussed. The author has doubts about accepting the "theory of ions," but suggests no substitute. Apparently he does not think that the recent study of solutions has added to our knowledge of the atom. He likewise (Chap. VIII) questions the views of J. J. Thomson in regard to electrons and leaves unmentioned the most remarkable contribution that has recently been made to our knowledge of the atom.[1] In the chapter on "Valence," Werner's hypothesis is disposed of in a page and a half, and Richards' work in fifteen lines. Speaking of the changes in valence by light, heat, and other agencies, the following is the whole account of the effect of electricity: "Changes of valence due to electricity are not unusual. Thus we have the production of carbon monoxide from carbon dioxide by the passage of the electric spark, $CO_2 = CO + O$. In general such changes may be attributed to chemical action induced by the electricity serving as the direct agent. The change may be the result of changed vibration or to changes of electrical state." Surely the electrolytic oxidations and reductions would have offered far more instructive, not to say convincing, illustrations. Much of the book seems to lack force in the same

[1] J. J. Thomson: *Phil. Mag.*, March, 1904.

way that this passage does. A chapter on "Molecules and the Constitution of Matter" concludes the volume.

The reviewer does not feel that the author has shown that the atomic theory, as it was twenty-five years ago, is a satisfactory medium for conveying modern views on such parts "of chemical theory * * * as bear directly upon the question of the constitution of matter."—*Preface.*

The author does not seem to favor modern views in regard to the methodology of science, a fact which, in a work dealing with a subject like this, necessarily shows itself in almost every sentence.

A. S.

KRITISCHE STUDIEN ÜBER DIE VORGÄNGE DER AUTOXYDATION. By C. ENGLER AND J. WEISSBERG. Vieweg und Sohn, Braunschweig, 1904. 197 pp. Price, 6 marks.

The two sides of the great problem of autoxidation or slow combination of compounds with oxygen at ordinary temperatures, are first the study of the mechanism of the processes in a qualitative sense, and second, the study of the dynamics of the reactions in a quantitative way in definite mathematical terms. In regard to the first of these problems the numberless theories that have been presented may be called variations, modified in details only, of two fundamental theories, those of C. F. Schönbein and of Moritz Traube. Schönbein believed that he had shown that ordinary oxygen must break down before it can oxidize any substance, into two oppositely polarized active modifications of oxygen, "ozone" and "antozone". In its more modern garb, this theory is that of the dissociation of the oxygen molecule into oppositely charged atoms or ions, $\overset{+\,+}{O}$ and $\overset{-\,-}{O}$, van't Hoff being the most prominent supporter of this view. According to Traube, on the other hand, oxidation is effected by the addition of atoms or radicals to the unsaturated molecule of oxygen, without any preliminary complete dissociation of the oxygen molecule, peroxides, R_2O_2, invariably resulting as primary oxidation products. Professor Engler, of the Polytechnische Hochschule in Karlsruhe, has made important original contributions supporting and modifying in some details Traube's views, and the present book is intended chiefly to arrange and discuss systematically all the more important oxidation processes from the point of view of the addition of molecular oxygen.

Although it appears not at all unlikely and not without precedent that oxygen may, according to conditions of concentrations and speeds of reactions, sometimes enter into combination through free valences of molecular oxygen, sometimes through atomic or ionic oxygen, the last, and probably the lesser product of progressive dissociation, according to

$$O_2 \rightleftarrows \overset{+\,+\quad --}{-O-O-} \rightleftarrows O + O,$$

so that both theories may ultimately prove to be well-founded, nevertheless to-day Traube's theory is much the stronger of the two on the basis of experimental evidence, and many important oxidation processes have been proved to conform to it and others, such as the combustion of hydrogen in the oxy-hydrogen flame, are possibly processes of the same kind. Under these circumstances Engler and Weissberg's book is a timely and valuable summary and elucidation of a mass of facts and observations from the point of view of the predominant theory. It is to be hoped that we shall soon have an equally good book bringing together the investigations on the second great problem of oxidation, its dynamics, especially from the point of view of physico-chemical measurements of oxidation cells, free energy and the catalysis of oxidation reactions. JULIUS STIEGLITZ.

ELECTROCHEMISTRY. BY R. A. LEHFELDT. New York: Longmans, Green and Co. 1904. 268 pp. Price, $1.60.

This forms one of the eight text-books on Physical Chemistry edited by Sir William Ramsay.

Chapter II, on "The Relation of Chemical Constitution to Conductivity", was ably prepared by T. S. Moore and is very complete in itself.

The book as a whole is very carefully written by authors who show that they are perfectly familiar with the developments of the science. The work fulfils to the letter the wish of the editor of the series, that the subject be brought up to date. It is properly confined to the principles and theories of electrochemistry. Matters pertaining more particularly to other physical properties, such as osmotic phenomena, etc., are briefly but clearly touched upon. The technical side of the subject is also not given much weight.

The work has been well prepared for students and investigators, as distinct from readers and experimenters, and it covers practically

all the important work on this portion of Physical Chemistry, both theoretical and experimental, which has been published.

The thermodynamic principles and the dependent calculations of the electromotive force of cells are very clearly given and illustrated. It might be considered bold to introduce some of the present theoretical work into a so-called text-book, such, for example, as the electron theory, which has been advanced so rapidly by the work of J. J. Thomson in connection with conductivity in gases, and that of Drude in the case of metallic coduction, but the reviewer believes that the way in which these subjects are treated could hardly be improved, and that in the use of the book students cannot fail to be attracted by the complaisant fearlessness of the author. This will do much to advance the correct and to correct the imperfect in recent theories. A few useful tables have been appended to the work.

The text-book should be a very satisfactory one for use in classes in electrochemistry. It is certainly sufficiently advanced and completely put together to satisfy the needs of the most advanced classes studying this subject. W. R. WHITNEY.

TEXT-BOOK OF GENERAL PHYSICS FOR HIGH SCHOOLS AND COLLEGES. By JOSEPH S. AMES, PH.D., Professor of Physics and Director of the Physical Laboratory in the Johns Hopkins University. The American Book Company, 768 pp. Price, $3.50.

Professor Ames gives us in this volume an excellent text-book written in the conviction "that the most important element in a course of instruction in physics is a text-book which states the theory of the subject in a clear and logical manner so that recitations may be held on it." In the opinion of the reviewer the "attempt to give a concise statement of the experimental facts on which the science of Physics is based, and to present with these statements the accepted theories which correlate or 'explain' them" is eminently successful. The book is a good specimen of the bookmaker's art and is remarkably free from errors of all kinds. A few inaccuracies of statement, however, have been noticed. Referring to p. 246, it may be said that the ordinary method of obtaining solid carbon dioxide is to invert the cylinder and allow the liquid to escape. The triple point for carbon dioxide is about —57° and 5 atmospheres pressure, whence it follows that —80° cannot, as has been done on p. 276, be said to be the boiling-point of the liquid.

It is suggested that in view of its greater simplicity and its much greater efficiency, at least for the smaller machines, a description of the Hampson apparatus for the liquefaction of air might advantageously have taken the place of one of the two given on pp. 280-281. Referring to p. 284, it is hardly true to say "that the whole science of Physical Chemistry" is based on the assumption of electrically charged ions. E. C. FRANKLIN.

A TEXT-BOOK OF PHYSIOLOGICAL CHEMISTRY. BY OLOF HAMMARSTEN. Authorized translation by JOHN A. MANDEL. Fourth American Edition. 8vo. viii + 703 pp. New York: John Wiley & Sons. Price, $4.00.

This translation is from the 5th German edition which appeared in March, 1904. The latter was called for by reason of the rapid advances recorded in physiological chemistry in the last four years, advances indicated by the success attending the publication of the new journals and reviews devoted to this special field. The appearance of the "Biochemisches Centralblatt," the "Beiträge zur chemischen Physiologie und Pathologie" and the "Ergebnisse der Physiologie" show beyond question the remarkable development of chemistry in its relations to medicine. The new edition of Hammarsten's work contains many things not in the old and in the selection of material from the enormous store available shows a success consistent with the reputation of the author. Even some of the latest discussions of the attempts at protein synthesis are fully considered.

The translator has apparently done his work well, as the English is smooth and straightforward. Certain blemishes in the earlier editions have been corrected in this. Beyond question this work is the most valuable book of the kind in our language. One of its greatest merits is its fairness, but it is just this which renders its use as a text-book in American medical schools somewhat problematical. Many of the discussions in physiological chemistry are still far from settled and in a fair treatment of these the author must present all sides deserving a hearing. This Hammarsten does admirably but the seeming contradictions are often very confusing to the student, especially to the beginner, and most of our students who use the work never pass beyond the beginner stage. Under the conditions which prevail in most of our schools of medicine the Hammarsten should be employed as a work of reference and for this purpose, with its many literature citations, it is

most excellent. Perhaps some day, when our medical schools make much stronger entrance requirements, books of this class may be more satisfactorily used and appreciated. J. H. LONG.

THE URINE AND CLINICAL CHEMISTRY OF THE GASTRIC CONTENTS, THE COMMON POISONS, AND MILK. By J. W. HOLLAND, M.D. Philadelphia: P. Blakiston's Son & Co. 172 pp. Price, $1.00.

This book contains the usual routine exercises given to students of medicine in many of the institutions of the country. Ninety-four pages treat of the urine, 21 pages of the gastric contents, 37 pages of poisons and 20 pages of milk. The descriptions of the various reactions and tests given are in the main satisfactory, but in the discussion of quantitative processes the explanations are too brief to give the student any real understanding of principles. In explaining the Fehling and Pavy sugar titrations the author speaks (p. 60 and p. 61) of the necessity for quick work and prompt end readings "as the test solution on standing takes up copper and turns blue again." Doubtless the taking-up of oxygen is intended. To the reviewer it has appeared for years that most of our books for medical students attempt to cover too many topics in very brief space. J. H. LONG.

APPLICATION OF SOME GENERAL REACTIONS TO INVESTIGATIONS IN ORGANIC CHEMISTRY. By DR. LASSAR-COHN, Professor of Organic Chemistry at the University of Königsberg. Authorized translation by J. BISHOP TINGLE, PH.D. 12mo. vii + 101 pp. Cloth, $1.00. New York: John Wiley & Sons. London: Chapman & Hall, Limited. 1904.

In the introductory chapter the author speaks as follows: "The time has arrived when it is possible to formulate, for the conduct of some operations, a number of general rules derived from the enormous mass of experimental material which has accumulated, and, as a corollary, to develop considerably many methods which are in use for organic chemical investigations. It may be hoped that, in course of time, the blind, trial and failure process may be increasingly restricted, and this little book is offered as an attempt to systematize methods of work." The subject-matter is arranged in four chapters. I, Introductory; Fixation of Labile Hydrogen Atoms. II, Modification of Reactions. III, Improvement in the Conditions of Reaction; Overstrain of Reactions. IV, Influence of Neighboring Atoms and Atomic Complexes.

To a certain extent the book may be regarded as a digest of the

author's larger work on organic laboratory practice, the great variety of new methods there set forth being here, as it were, grouped under a few general headings, to show their logical connection with the underlying theoretical considerations involved. The subject is treated in a broad and comprehensive way, and attention is frequently called to points where further experimental data are needed. No one directing research work in Organic Chemistry can afford to be without this little book, for a careful perusal of its pages will not only show, in many cases, how a troublesome reaction may be made more efficient, or success obtained instead of failure, but it may also prevent the loss of much valuable time due to using, at the outset, an inferior process or one foredoomed to failure.

The work of the translator is, on the whole, acceptably done, and all organic chemists who do not read German should be grateful to Dr. Tingle for this service. In one or two places, however, the meaning is rather obscure. Thus, the opening sentence in the first chapter reads as follows: "All investigations in the domain of organic chemistry are based, in the firmest and most complete manner, on those parts of general theory which apply to the carbon atom, but only a comparatively small number of them retain these higher and more exhaustive points of view in the experimental portions of the work."

The book is neat and attractive in appearance, of convenient size, clearly printed with good type on a good quality of paper. Typographic errors are few. Only one is likely to cause any confusion in the mind of the hasty reader, and that is on page 25, line 6 from the top, where "phenylacetic" appears instead of "phthalylacetic."

M. T. BOGERT.